

1965

The chemistry and transition metal complexes of 2,8,9-trioxa-1-phospha-adamantane

Thomas Joseph Huttemann Jr.
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THE CHEMISTRY AND TRANSITION METAL
COMPLEXES OF 2,8,9-TRIOXA-1-PHOSPHA-
ADAMANTANE.

Iowa State University of Science and Technology,
Ph.D., 1965
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THE CHEMISTRY AND TRANSITION METAL COMPLEXES OF
2,8,9-TRIOXA-1-PHOSPHA-ADAMANTANE

by

Thomas Joseph Huttemann, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Of Science and Technology
Ames, Iowa

1965

TABLE OF CONTENTS

	Page
HISTORICAL	1
STATEMENT OF THE PROBLEM	3
MODE OF ATTACK	8
EXPERIMENTAL	11
Instrumentation and Apparatus	11
Ligand IV and Derivatives	14
Coordination Compounds of IV	19
The Hydrolysis Product of IV (IVH ₂ O) and Coordination Compounds of IVH ₂ O	28
Uncharacterized Complexes of IV	31
Coordination Compounds of Open-Chain Trialkyl Phosphites	34
Uncharacterized Complexes and Attempted Prepara- tions of Open-Chain Trialkyl Phosphites	35
Physical Measurements	38
DISCUSSION	54
2,8,9-Trioxa-1-phospha-adamantane (IV)	54
Michaelis-Arbuzov Reactions of IV	64
Phosphonium Salts of IV	73
Transition Metal Complexes of IV	78
Transition Metal Complexes of Open-Chain Trialkyl Phosphites	88

TABLE OF CONTENTS (continued)

	Page
AREAS FOR FURTHER INVESTIGATION	90
Ligand IV and Derivatives	90
Transition Metal Complexes of IV	90
Transition Metal Complexes of Open-Chain	91
Trialkyl Phosphites	
The Arsenic Analog of IV	92
LITERATURE CITED	94
ACKNOWLEDGMENT	100
VITA	102

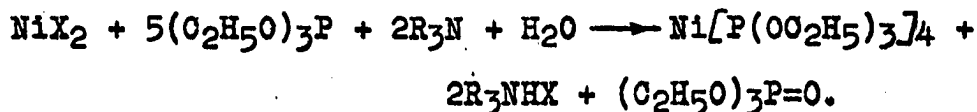
HISTORICAL

A survey of the literature indicates that relatively few investigations have been reported involving the use of trialkyl phosphites as ligands, particularly with respect to transition metal ions. Although the reactions of various first row transition metal halides with a number of trialkyl phosphites have been studied, only the copper(I) and nickel(0) complexes reported in Table 1 have been isolated.

Table 1. Transition metal complexes of open-chain trialkyl phosphites

Compound	Comment	Reference
$\text{CuX} \cdot \text{P}(\text{OR})_3$	$\text{X} = \text{Cl, Br; R} = \text{Me, Et, iso-Pr, Ph}$	1-3
	$\text{X} = \text{I; R} = \text{Et}$	2
	$\text{X} = \text{CN; R} = \text{Me, Et, iso-Pr}$	4, 5
$\text{CuX} \cdot \text{P}(\text{OR})(\text{OCMe}_2\text{CCl}_3)_2$	$\text{X} = \text{Cl; R} = \text{Me, Et, iso-Pr, n-Pr, iso-Bu, n-Bu}$	6
$\text{CuX} \cdot 2\text{P}(\text{OR})_3$	$\text{X} = \text{CN; R} = \text{Me, Et, iso-Pr, n-Pr, n-Bu, Ph}$	4, 5
$\text{Ni} \cdot 4\text{P}(\text{OR})_3$	$\text{R} = \text{Me, Et, Ph, 2-ethyl-hexyl, decyl, 2-chloroethyl, p-methoxyphenyl, p-tolyl}$	7-11
$\text{Ni} \cdot 2\text{P}(\text{OR})_3 \cdot 2\text{P}(\text{OR}')_3$	$\text{R} = \text{Ph; R}' = \text{Et}$	10
$\text{PtX}_2 \cdot 2\text{P}(\text{OR})_3$	$\text{X} = \text{Cl; R} = \text{Me, Et}$	12-14
$\text{Pt} \cdot 4\text{P}(\text{OR})_3$	$\text{R} = \text{Ph, p-chlorophenyl}$	15
$\text{Pd} \cdot 4\text{P}(\text{OR})_3$	$\text{R} = \text{Ph}$	16, 17
$\text{AgX} \cdot \text{P}(\text{OR})_3$	$\text{X} = \text{Cl; R} = \text{Me, Ph}$	1, 18
$\text{AuX} \cdot \text{P}(\text{OR})_3$	$\text{X} = \text{Cl; R} = \text{Me, Ph}$	1, 18

Most of the copper(I) complexes were prepared by refluxing the metal salt and liquid trialkyl phosphite in a solvent such as benzene, or carrying the reaction out neat, filtering any solid formed, and concentrating the solution under vacuum to obtain the solid product in 90-100% yield. The complexes were then purified by recrystallization from suitable solvent systems. The majority of nickel(0) complexes were prepared from either $\text{Ni}(\text{CO})_4$ or a substituted nickel carbonyl. Recently Vinal and Reynolds (8) synthesized $\text{Ni}[\text{P}(\text{OR})_3]_4$ ($\text{R} = \text{Me}, \text{Et}$) using a method represented by the reaction



Many of the copper compounds are postulated to have dimeric and trimeric structures from molecular weight studies. In a report of the reaction of cobalt, nickel and iron halides it was concluded that no complexes could be isolated with various ligands of the type $(\text{RO})_3\text{P}$ (1).

Other metal coordination compounds involving trialkyl phosphites as ligands include complexes of $\text{Pt}(\text{II})$, $\text{Pt}(\text{O})$, $\text{Pd}(\text{O})$, $\text{Ag}(\text{I})$ and $\text{Au}(\text{I})$; these are also presented in Table 1. The only other area where trialkyl phosphites have been used to any extent as ligands is in substituted carbonyl and nitrosyl complexes. An excellent review of the literature on substituted carbonyls with phosphorus-containing ligands can be found in the Ph.D. thesis of D. G. Hendricker (19).

STATEMENT OF THE PROBLEM

The purpose of this investigation was to study the nature of transition metal complexes in various oxidation states employing a unique monodentate ligand containing phosphorus as the donating atom. The coordinating power of a ligand will be determined by (a) the nature of the donating atom, (b) the electronegativity of the groups attached to the donating atom, and (c) the size and mobility of the groups attached to the donating atom.

The nature of the donating atom is the predominant factor which determines its Lewis basicity as well as its ability to pi-bond with another atom or molecule. Those molecules which are good Lewis bases might be expected to form complexes with transition metals. If the donor atom has empty d-pi orbitals suitably low in energy, then back acceptance of electron density from the filled d orbitals of the metal is conceivable as shown in Figure 1. The availability of these d orbitals

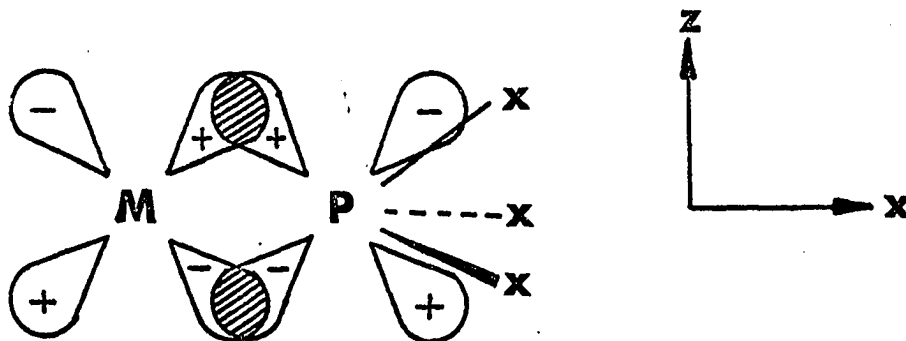
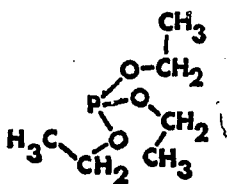


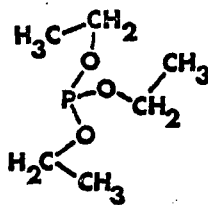
Figure 1. D-pi d-pi bonding in a M-P bond

on the donor atom is very much influenced by the electronegativity of the groups attached to the donor atom. Although highly electronegative groups bonded to the donor atom will lower the electron density of the lone pair electrons resulting in a decrease in donor strength, the possibility of withdrawing d-orbital electron density from the metal into the unoccupied d orbitals of the donor atom in the ligand is increased. Hence the ligand-metal bond may be composed of two contributions; sigma-bonding from the ligand to the metal and back pi-bonding from the metal to the donor atom.

The size and mobility of the groups attached to the donating atom could possibly affect the coordination properties of a ligand. For example in triethyl phosphite the alkoxy groups are free to rotate and, therefore, can possibly sterically hinder coordination to a metal atom. This can be seen in the schematic drawings I and II. The use of scale models readily



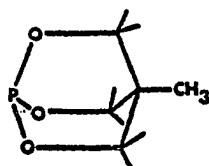
I



II

shows that there are few configurations which the alkoxy groups can assume leaving the electron pair on the phosphorus exposed for donation. The alkoxy groups are also able to interact sterically with one another thereby preventing the maximum coordination number of the metal ion from being attained with these ligands.

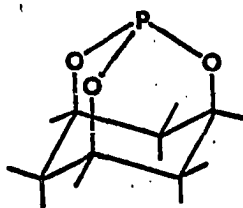
When the above three criteria for a good coordinating ligand are considered, it might be expected that constraint of the alkoxy moiety in trialkyl phosphites would afford such a model ligand. The constrained phosphite ligand, 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2,2,2]octane (III), was prepared by J. G. Verkade (20), and was shown to have excellent coordination properties (21-23). Transition metal complexes of copper(I), silver(I), gold(I), palladium(II), platinum(II), cobalt(I), cobalt(III), nickel(II) and nickel(0) were prepared. In most instances maximum coordination was exhibited with only the phosphite ligand in the coordination sphere.



III

Ligand III has been shown to be a considerably better Lewis base than open-chain phosphites in a study of the one to one complexes formed with the acids BH_3 , $\text{B}(\text{CH}_3)_3$ and BF_3 (24-27). It has also been shown that the CO bond has a higher force constant in substituted metal carbonyls than in any other metal carbonyl reported (28) possessing a phosphorus-containing ligand. The latter result was interpreted to arise from a substantial degree of d-pi d-pi bonding in the M-P bond (28).

Another constrained phosphite ester whose donor properties were investigated to some extent is 2,8,9-trioxa-1-phospha-adamantane (IV). This compound was first synthesized by H. Stetter and K. Steinacker in 1952 (29) by reacting PCl_3 with cis-1,3,5-trihydroxycyclohexane in tetrahydrofuran in the presence of pyridine. The tricyclic phosphite ligand IV has been shown to be a slightly better Lewis base than III toward a number of boron Lewis acids (25).



IV

As the literature is void of information concerning the coordination of trialkyl arsenites, it became of interest to prepare the previously unknown arsenic analog of IV, and to study any isolable transition metal complexes of this ligand.

MODE OF ATTACK

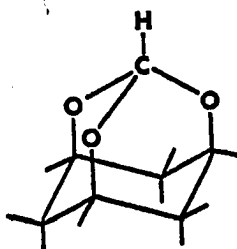
In order to extend the investigations of constrained phosphite esters as donors by the use of IV, it was necessary to prepare this compound in sufficient yield to be feasibly used as a ligand. The chemical and physical properties of IV were to be extensively investigated as well as the nature of any isolable transition metal complexes in various oxidation states. The transition metal complexes of IV could then be compared with those of III, and perhaps the effect of the increased bulk of IV could be revealed.

In order to study the nature of the electronic environment on the phosphorus atom, especially when in a four-coordinate state as is the case upon complexation, the phosphate and thiophosphate derivatives of IV were to be made as well as stable phosphonium salts formed from various organic carbonium perchlorates or tetrafluoroborates. In this way a comparison could be made between the n.m.r. spectra of IV in its transition metal complexes, chalcogenates, and phosphonium salts, in which the phosphorus atom is tetravalent in all cases. The effect of a positive charge on the proton chemical shifts of the base moiety could then be ascertained for the chalcogenates and phosphonium salts in the absence of influences stemming from the more complex geometries of the metal complexes formed with this polycyclic ligand.

For the comparison of the n.m.r. spectra of IV and its

compounds, an unambiguous assignment of the H^1 spectrum of IV became desirable. Even though the axial and equatorial hydrogens are chemically different by geometry, they are attached to the same carbon atom. It is not possible to assign the chemical shifts to these protons in the n.m.r. spectrum of IV since there is no qualitative way to determine which proton is less electronically shielded.

From a knowledge of the dipole moment, its direction and approximate location in an organic molecule, Buckingham (30) has been able to predict consequent chemical shifts of the various protons relative to those in the nonpolar parent molecule. In order to unambiguously assign the nuclear magnetic resonance absorptions of the axial and equatorial hydrogens observed for IV, Buckingham's approach was to be undertaken. It was possible to tentatively assign the axial and equatorial proton absorptions in the n.m.r. spectrum of IV by employing a spin decoupling technique and by comparing the proton n.m.r. spectrum of the orthoformate of IV (V) with that of IV (27).



V

In order to evaluate the effect of steric hindrance in the formation of transition metal complexes with trialkyl phosphites, an attempt was to be made to prepare complexes with transition metal ions using open-chain phosphites such as trimethyl, triethyl, triisopropyl, tributyl and triphenyl phosphite. To reduce complications due to anion coordination, metal perchlorates were to be employed in the form of aquo or dimethylsulfoxato complexes.

In addition to elemental analyses, further characterization of all of the compounds isolated were to be accomplished where feasible by dipole moment, infrared spectral, proton and phosphorus nuclear magnetic resonance spectral, visible and ultraviolet spectral, magnetic susceptibility and molar conductivity studies.

EXPERIMENTAL

Instrumentation and Apparatus

Infrared spectra

Infrared spectra in the sodium chloride region were obtained in nujol and hexachlorobutadiene mulls and in KBr pellets on a Perkin-Elmer Model 21 spectrometer.

Visible and ultraviolet spectra

Spectra were obtained in the visible and ultraviolet regions on a Beckman DK-2A recording spectrophotometer and on a Cary Model 14 spectrophotometer.

Nuclear magnetic resonance spectra

Proton n.m.r. spectra were obtained on approximately 5 to 30% by weight solutions on a Varian HR-60 n.m.r. spectrometer.

Molar conductivities

Conductivities were measured at 25°C with an Industrial Instruments Incorporated Model RC-16B2 conductivity bridge at 1000 c.p.s. The cell employed had a cell constant of 0.077 cm.⁻¹ and measurements were taken on approximately 0.001 molar solutions. All of the conductivities were measured in conductivity water, acetonitrile, or acetone. All of the solvents were reagent grade. The acetonitrile was further purified by refluxing over phosphorus pentoxide for 3 hr. followed by distilling at atmospheric pressure, and the acetone was further dried by storing over Linde 4-A molecular sieve.

Dipole moments

The dielectric constant apparatus used to measure the capacitances of the sample solutions was a Sargent Model V Oscillometer. The commercial cell and cell holder were mounted in a copper can which was submerged in a constant temperature bath maintained at a temperature of $25.00 \pm 0.05^{\circ}$. The solvents used were purified by fractional distillation from Na, LiAlH_4 , CaH_2 or P_2O_5 ; the purity was checked on a Perkin-Elmer Model 154 Vapor Fractometer. The cell was calibrated using these solvents and their dielectric constants obtained from the literature (31-34).

The indices of refraction of the standards and solutions were measured with a Bausch and Lomb refractometer using polychromatic light adjusted to the Na_D line by means of a compensator. The instrument was calibrated using a solid test piece of known refractive index.

Most of the original solutions were prepared under anaerobic conditions using a vacuum line. The original solutions were then diluted and the mole fractions calculated from a knowledge of the weight of the new solution before and after dilution and of the mole fraction of the original solution. The capacitances of the solutions were then measured and the dielectric constants obtained from standard curves.

The orientation polarization, P_o , of the solute molecule was calculated using the Cohen Henriquez equation,

$$P_0 = \frac{3My}{dy(n_{\infty}^2 y + 2)^2} \left[\frac{d\epsilon}{dx} - 2(n_{\infty}) \frac{dn_{\infty}}{dx} \right]$$

where My , dy and $n_{\infty}y$ are the molecular weight, density and index of refraction at infinite wave length of the solvent, respectively (35). If slightly polar solvents were used, the term $(n_{\infty}^2 y + 2)$ was replaced by $(\epsilon y + 2)$ using the Maxwell relationship, $\epsilon = n^2$ (36). It was also assumed in the calculations that $\frac{dn_{\infty}}{dx} = \frac{dn_D}{dx}$. The dipole moment was then calculated using the Debye equation,

$$\mu = \sqrt{\frac{9kTP_0}{4\pi N}}$$

where μ is the dipole moment, k is the Boltzmann constant, T is the absolute temperature, and N is Avogadro's number (35). The quantities $\frac{d\epsilon}{dx}$ and $\frac{dn_D}{dx}$ were calculated from a least squares treatment of the data obtained from a plot of ϵ against x and n against x .

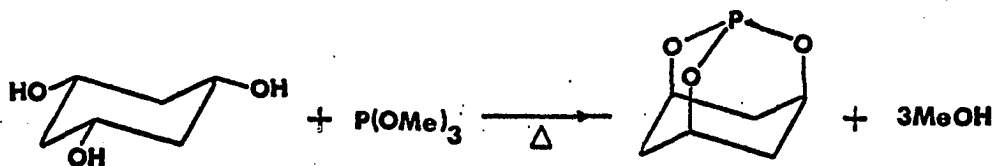
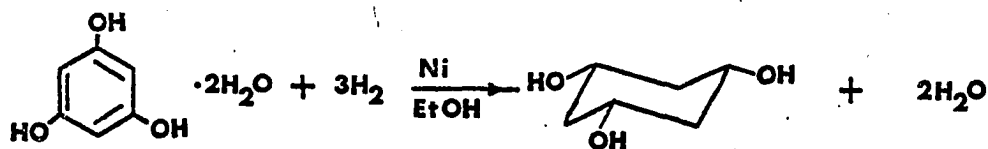
Magnetic susceptibilities

The magnetic susceptibility measurements were carried out on a Faraday balance by Dr. T. S. Piper of the University of Illinois. All of the complexes measured were shown to be diamagnetic at room temperature. The fact that the nuclear magnetic resonance spectra of these complexes could be obtained was also a good indication of their diamagnetism.

Ligand IV and Derivatives

2,8,9-Trioxa-1-phospha-adamantane (IV)

The polycyclic phosphite was first synthesized by Stetter and Steinacker in 1952, and involved treating cis-1,3,5-cyclohexanetriol with phosphorus trichloride in tetrahydrofuran. The cis-triol was prepared by hydrogenating an ethanolic solution of phloroglucinol-dihydrate employing a Raney nickel catalyst at atmospheric pressure and 50°. The yield using this method was only 20%. The method employed in this investigation involved refluxing a mixture of the cis-triol in a 4.5 mole excess of trimethyl phosphite for $\frac{1}{2}$ hr. beyond the dissolution of the triol. The methanol that formed and the excess trimethyl phosphite were then evaporated from the solid cage phosphite under vacuum at 70 to 80°. The crude product was then purified by sublimation at 0.02 mm. pressure and 80°, whereupon a 70% yield was obtained. The colorless solid is soluble in most organic solvents, is slowly hydrolyzed and has a melting point of 208-209° (37).



2,8,9-Trioxa-1-phospha-adamantane-1-oxide

The phosphate ester was prepared by treating an ethanolic solution (0.08 g./ml.) of the phosphite with an equimolar quantity of 30% hydrogen peroxide in an exothermic reaction. Colorless crystals slowly formed as the solution cooled to room temperature. The product obtained in this manner was quite pure, but further purification was accomplished by recrystallization from n-butanol or dioxane in 97.8% yield. The phosphate ester is soluble in water, methanol, and ethanol, slightly soluble in dioxane, chloroform and n-butanol, insoluble in ether and benzene and has a melting point of 275° (literature: 268° (29)).

2,8,9-Trioxa-1-phospha-adamantane-1-sulfide

An intimate mixture of 1.60 g. (10.0 mmole) of IV and 0.32 g. (10.0 mmole) of sulfur powder was heated in an oil bath to 150° and held at this temperature for 10 min. After the fused mass had cooled to room temperature, it was extracted with CS₂ to remove any unreacted sulfur, and then purified by sublimation at 0.02 mm. pressure and 190°. The colorless solid is soluble in chloroform, acetone and benzene, slightly soluble in ethanol, methanol, and dioxane, insoluble in water and ether, and has a melting point of 250-251° (literature: 250-251° (29)).

1-Triphenylmethyl-2,8,9-trioxa-1-phospha-adamantane perchlorate

To a solution of 2.27 g. (8.16 mmole) of chlorotriphenyl

methane in 15 ml. of acetone was added a solution of 1.00 g. (8.16 mmole) of sodium perchlorate in 10 ml. of acetone. After a period of 5 min. the sodium chloride was filtered and the supernatant allowed to pass into a solution of 1.30 g. (8.16 mmole) of IV in 10 ml. of acetone. The light yellow powder which slowly formed over a period of 12 hr. was filtered and dried under vacuum at room temperature. Upon recrystallization from boiling acetonitrile, 4.10 g. (100% yield) of colorless crystals were obtained having a melting point of 183°.

Anal. Calcd.: C, 59.6; H, 4.82. Found: C, 60.5;
H, 5.08.

1-Triphenylmethyl-2,8,9-trioxa-1-phospha-adamantane tetrafluoroborate

To a solution of 1.43 g. (5.12 mmole) of chlorotriphenyl methane in 15 ml. of acetone was added a solution of 1.00 g. (5.12 mmole) of silver tetrafluoroborate in 10 ml. of acetone. After a period of 5 min. the silver chloride was filtered and the supernatant allowed to pass into a solution of 0.82 g. (5.12 mmole) of IV in 10 ml. of acetone. The colorless crystals that formed were filtered under nitrogen and dried under vacuum at room temperature. A total of 2.00 g. (80% yield) of solid was collected which was recrystallized from boiling acetone. The recrystallized product has a m.p. of 190°.

Anal. Calcd.: C, 61.1; H, 4.95. Found: C, 61.8;
H, 5.16.

1-Ethyl-2,8,9-trioxa-1-phospha-adamantane tetrafluoroborate

To a solution of 2.60 g. (1.37 mmole) of triethyloxonium tetrafluoroborate in 10 ml. of methylene chloride was added 4.38 g. (2.74 mmole) of IV in 10 ml. methylene chloride. The colorless solution was allowed to stand 3 hr. at room temperature. Cooling to -10°C resulted in the formation of colorless crystals which were washed three times with 100 ml. portions of carbon tetrachloride and subjected to vacuum drying at room temperature for 1 hr. A 75% yield was realized; the solid has a m.p. of $115-117^{\circ}$.

3- α -Oxo-3- β -benzyl-7- α -p-toluenesulfonylmethyl-2,4-dioxa-3-phosphabicyclo[3.3.1] nonane

A mixture of 2.62 g. (10.0 mmole) of benzyl-p-toluenesulfonate and 1.60 g. (10.0 mmole) of IV was heated in an evacuated sealed tube at 85° for 6 hr. The resulting colorless solid was recrystallized in 21% yield from methanol and has a m.p. of 168° .

Anal. Calcd.: C, 57.08; H, 5.55. Found: C, 56.82;
H, 5.45.

3- α -Oxo-3- β -triphenylmethyl-7- α -chloro-2,4-dioxa-3-phosphabicyclo[3.3.1] nonane

Method (A): A mixture of 1.60 g. (10.0 mmole) of IV and 2.79 g. (10.0 mmole) of chlorotriphenyl methane was melted in an evacuated sealed tube at 155° for 16 hr. A 43% yield of colorless crystals having a decomposition point of 259° was collected after recrystallizing the crude product from

boiling benzene.

Anal. Calcd.: C, 68.5; H, 5.52. Found: C, 68.5;
H, 5.39.

Method (B): To a solution of 0.80 g. (5.00 mmole) of IV in 10 ml. of acetonitrile was added a solution of 1.39 g. (5.00 mmole) of chlorotriphenyl methane in 20 ml. of acetonitrile. A total of 2.00 g. (92% yield) of colorless crystals was collected upon allowing the solution to evaporate slowly. The compound was identical to that prepared by method (A) as shown by its decomposition point and proton n.m.r. spectrum.

2.8.9-Trioxa-1-arsa-adamantane

Tetrahydrofuran was distilled after refluxing over lithium aluminum hydride for 2 hr. The portion boiling from 65-66° was collected. Pyridine was purified by refluxing over barium oxide for 24 hr. followed by distillation.

In a 3-neck 1-liter flask equipped with a true bore stirrer and two 125 ml. addition funnels was placed 300 ml. of tetrahydrofuran and 10 g. (75.8 mmole) of 1,3,5-trihydroxycyclohexane. The system was then flushed with dry nitrogen and kept under a positive pressure of nitrogen. In one addition funnel was placed 18.35 ml. (227.4 mmole) of pyridine diluted to 50 ml. with tetrahydrofuran, and in the other addition funnel was placed 6.35 ml. (75.8 mmole) of arsenic trichloride diluted to 50 ml. with tetrahydrofuran. Both solutions were added dropwise over a period of 30 min. A

flocculent white solid, pyridinium chloride, formed immediately, but no heat was apparently generated by the reaction. The reaction mixture was stirred at room temperature for 2 hr. at which time a pink coloration was observed. The solution was decanted through pyrex wool and evaporated to dryness. The crude solid which remained was extracted with anhydrous ether and the ether extract evaporated to dryness. The residue was sublimed at 0.02 mm. pressure and 70°. A total of 9.10 g. (59% yield) of colorless crystals was collected. The polycyclic arsenite is soluble in most organic solvents, is decomposed by water, and has a melting point of 215-216°.

Anal. Calcd.: C, 35.32; H, 4.45. Found: C, 35.62;
H, 4.53.

Coordination Compounds of IV

Cu(ClO₄)·4IV

To a stirred solution of 0.37 g. (1.0 mmole) of Cu(ClO₄)₂·6H₂O in 10 ml. of absolute ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 25 ml. of absolute ethanol. A colorless solid formed immediately. The solution was cooled to 0° for 1 hr., after which the solid was filtered under nitrogen, washed with two 3 ml. portions of ethanol and two 3 ml. portions of anhydrous ether, and dried under vacuum at room temperature. A total of 0.75 g. (94% yield) was collected. The complex is soluble in water and acetonitrile and is insoluble in most other organic solvents.

Anal. Calcd.: Cu, 7.92; C, 36.00; H, 4.49; Cl, 4.42.

Found: Cu, 8.34; C, 35.58; H, 4.52; Cl, 4.27.

Cu(NO₃)·4IV

To a stirred solution of 0.48 g. (2.0 mmole) of Cu(NO₃)₂·3H₂O in 10 ml. of absolute ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 25 ml. of absolute ethanol. A colorless solid formed immediately. The solution was stirred for 1 hr. and then cooled to 0°. The complex was filtered under nitrogen, washed with two 3 ml. portions of cold ethanol and two 3 ml. portions of anhydrous ether, and dried under vacuum at room temperature. A total of 1.52 g. (99% yield) was collected. The complex is soluble in water, acetonitrile and methanol. The supernatant was evaporated to one-half volume and an equal volume of ether added. The resulting colorless solid was filtered and recrystallized from n-butanol. The melting point of the pure solid was 269° and its infrared spectrum was identical to that of the oxide of IV revealing the oxidation product in this reaction to be the phosphate ester.

Anal. Calcd.: Cu, 8.30; C, 37.70; H, 4.74; N, 1.83;

P, 16.20. Found: Cu, 8.48; C, 37.71; H, 4.80;

N, 1.88; P, 15.85.

Ag(ClO₄)·4IV

To a stirred solution of 0.21 g. (1.0 mmole) of AgClO₄ in 10 ml. of absolute ethanol was added a solution of 0.96 g. (6.0 mmole) of IV in 20 ml. of absolute ethanol. The colorless solid that formed immediately was filtered under nitrogen,

washed with two 3 ml. portions of cold ethanol and two 3 ml. portions of anhydrous ether, and dried under vacuum at room temperature. A total of 0.85 g. (100% yield) was collected. The complex is slightly soluble in acetonitrile, is insoluble in most other organic solvents, and decomposes in water.

Anal. Calcd.: Ag, 12.71; C, 34.05; H, 4.28; Cl, 4.19; P, 14.63. Found: Ag, 12.45; C, 34.01; H, 4.30; Cl, 4.10; P, 14.95.

Ag(NO₃)·4IV

To a stirred solution of 0.34 g. (2.0 mmole) of AgNO₃ in 50 ml. of absolute ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 25 ml. of absolute ethanol. The white crystals that formed were filtered under nitrogen, washed with two 3 ml. portions of cold ethanol and two 3 ml. portions of anhydrous ether, and dried under vacuum at room temperature. A total of 1.60 g. (99% yield) was collected. The complex was purified by recrystallization from dimethylsulfoxide, and is soluble in water and acetonitrile.

Anal. Calcd.: Ag, 13.30; C, 35.60; H, 4.48; N, 1.73; P, 15.30. Found: Ag, 13.25; C, 34.55; H, 4.56; N, 1.79; P, 15.50.

AuCl·IV

To a stirred solution of 0.97 g. (2.5 mmole) of HAuCl₄·3H₂O in 20 ml. of anhydrous ether was added a solution of 2.80 g. (17.5 mmole) of IV in 60 ml. of anhydrous ether. The solution, containing a light yellow solid which had formed

immediately, was cooled to 0° for 3 hr., filtered under nitrogen, washed with two 10 ml. portions of anhydrous ether, and dried under vacuum at room temperature. The solid was recrystallized from acetonitrile giving a total of 0.92 g. (94% yield) of colorless solid. The complex is insoluble in water and most organic solvents.

Anal. Calcd.: C, 18.38; H, 2.23; Cl, 9.02. Found:
C, 18.28; H, 2.27; Cl, 9.12.

Ni(ClO₄)₂·6IV

The starting material, Ni(ClO₄)₂·6DMSO, was prepared by a standard method (38). To a stirred solution of 0.75 g. (1.04 mmole) of Ni(ClO₄)₂·6DMSO in 25 ml. of acetone was added a solution of 1.00 g. (6.25 mmole) of IV in 10 ml. of acetone. The solution changed in color from light green to yellow immediately and a yellow solid formed. The mixture was stirred for 30 min. after which the solid was filtered under nitrogen, washed with two 5 ml. portions of cold acetone and two 5 ml. portions of ether, and dried under vacuum at room temperature. A total of 1.15 g. (91% yield) was collected. The complex can be recrystallized from acetone or methanol, is slightly soluble in ethanol and acetonitrile and decomposes slowly in water.

Anal. Calcd.: Ni, 4.82; C, 35.42; H, 4.47; Cl, 5.82.
Found: Ni, 4.85; C, 34.38; H, 4.55; Cl, 5.74.

(Ni·6IV)(Ni·4NO₃)

The starting material, Ni(NO₃)₂·6DMSO, was prepared by a

method described elsewhere (39). To a stirred solution of 0.65 g. (1.0 mmole) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{DMSO}$ in 25 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 8 ml. of acetone. The solution was stirred for 30 min. after which the yellow solid which formed during this time was filtered under nitrogen, washed with two 5 ml. portions of cold acetone, and dried under vacuum at room temperature. An 84% yield was realized. The complex was purified by recrystallizing from acetone, and was kept under an atmosphere of nitrogen since it is slightly hygroscopic.

Anal. Calcd.: C, 32.5; H, 4.10; N, 4.22. Found:

C, 30.42; H, 4.47; N, 4.43.

$\text{Ni}(\text{NO}_3)_2 \cdot 5\text{IV} \cdot \text{H}_2\text{O}$

To a stirred solution of 0.59 g. (2.0 mmole) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 10 ml. of absolute ethanol was added a solution of 1.92 g. (12.0 mmole) of IV in 25 ml. of absolute ethanol. There was an immediate color change from green to yellow, and a yellow powder was isolated upon the addition of ether. The solid was filtered under nitrogen, washed with ethanol and ether, and dried under vacuum at room temperature. A 100% yield (2.00 g.) was realized. The complex is soluble in most organic solvents and was purified by recrystallization from methanol.

Anal. Calcd.: Ni, 5.87; O, 35.91; H, 4.72; N, 2.80;

P, 15.40. Found: Ni, 5.80; O, 36.42; H, 5.20;

N, 2.54; P, 15.06.

Ni(ClO₄)₂·5IV·H₂O

To a stirred solution of 0.73 g. (2.0 mmole) of Ni(ClO₄)₂·6H₂O in 10 ml. of absolute ethanol was added a solution of 1.92 g. (12.0 mmole) of IV in 25 ml. of absolute ethanol. The yellow crystals which formed were filtered under nitrogen, washed with ethanol and ether, and dried under vacuum at room temperature. A total of 2.10 g. (97% yield) was collected. The complex is slightly soluble in and can be adequately recrystallized from acetone, ethanol and methanol. It is soluble in acetonitrile and decomposes in water.

Anal. Calcd.: Ni, 5.46; O, 33.52; H, 4.41; Cl, 6.59.

Found: Ni, 5.41; O, 33.55; H, 4.49; Cl, 6.58.

Ni·4IV

A mixture of 4.50 g. (4.19 mmole) of Ni(ClO₄)₂·5IV·H₂O and 0.70 g. (8.38 mmole) of NaHCO₃ in 15 ml. of water was heated on a steam bath for 5 min. beyond the disappearance of the yellow color of the starting nickel complex. A colorless solid formed and CO₂ was evolved. The solution was cooled to 0° for 2 hr., and the colorless crystals which formed were filtered, washed with two 5 ml. portions of water, and dried under vacuum at room temperature. A 99% yield was realized. The complex is insoluble in most common solvents but was recrystallized from boiling ethanol.

Anal. Calcd.: Ni, 8.39; C, 41.3; H, 5.20.

Found: Ni, 8.15; C, 40.57; H, 5.14.

PdCl₂·4IV·2H₂O

To a suspension of 0.36 g. (2.0 mmole) of PdCl₂·2H₂O in 75 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of acetone. The solution was stirred for 4 days after which the resulting off-white solid which formed was filtered and dried under vacuum at room temperature. A total of 1.62 g. (95% yield) was collected. The complex is insoluble in all organic solvents and decomposes in water.

Anal. Calcd.: C, 33.75; H, 4.73. Found: C, 33.59;

H, 4.61.

PtCl₂·2IV

The starting material, trans-PtCl₂(py)₂, was prepared by a method described elsewhere (40). To a stirred mixture of 0.88 g. (1.5 mmole) of trans-PtCl₂(py)₂ in 30 ml. of acetone was added a solution of 0.96 g. (6.0 mmole) of IV in 10 ml. of acetone. There was an immediate color change from light yellow to colorless and the odor of pyridine was evident. The solution, containing a colorless solid, was stirred for $\frac{1}{2}$ hr. after which the solid was filtered under nitrogen, washed with acetone and ether, and dried under vacuum at room temperature. Another fraction of white solid was obtained upon evaporation of the supernatant liquid to dryness. The total quantity of solid was extracted with boiling ethanol in which only part of it was soluble. A total of 0.62 g. (71% yield) of insoluble complex remained after drying under vacuum. Addition of ether to the ethanol extract produced 0.60 g. of unidentifiable

powder.

Anal. Calcd.: C, 24.60; H, 3.11; Cl, 12.09. Found:
C, 24.73; H, 3.20; Cl, 11.89.

Co(ClO₄)·5IV and Co(ClO₄)₃·6IV

To a stirred solution of 0.74 g. (2.0 mmole) of Co(ClO₄)₂·6H₂O in 15 ml. of acetone was added a solution of 3.20 g. (20.0 mmole) of IV in 15 ml. of acetone. There was an immediate color change from violet to yellow, and a mixture of white and yellow solid formed under a yellow supernatant. The mixture contained predominantly the colorless modification, which was shown to be Co(ClO₄)₃·6IV. After the solid was filtered, the yellow supernatant was evaporated to dryness and the resulting yellow solid recrystallized from methanol giving 0.84 g. (88% yield) of yellow Co(ClO₄)·5IV. The colorless modification was recrystallized from water to give 1.32 g. (100% yield) of white crystals. The monovalent cobalt complex is slightly soluble in acetone and ethanol, soluble in methanol and acetonitrile, and decomposes upon standing in water. The trivalent cobalt complex is slightly soluble in water and acetonitrile and is insoluble in most other common solvents.

Anal. Calcd. for Co(ClO₄)·5IV: Co, 6.15; C, 37.60;
H, 4.74; Cl, 3.70. Found: Co, 6.09; C, 37.55;
H, 4.86; Cl, 3.42.

Anal. Calcd. for Co(ClO₄)₃·6IV: Co, 4.47; C, 32.80;
H, 4.10; Cl, 8.08. Found: Co, 4.43; C, 32.51;

H, 4.20; Cl, 8.07.

Co(NO₃)₃·6IV and (Co·5IV)₂(Co·4NO₃)

To a stirred solution of 0.65 g. (1.0 mmole) of Co(NO₃)₂·6DMSO (39) in 15 ml. of absolute ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 15 ml. of ethanol. The solution was stirred for 1 hr., evaporated to one-half the volume, and an equal volume of ether added yielding a light pink curdy solid under a pink supernatant. The solid was filtered under nitrogen and washed with five 5 ml. portions of acetone leaving the solid almost colorless. The white solid was then recrystallized three times from absolute ethanol to give colorless crystals which were filtered under nitrogen and dried under vacuum at room temperature. A yield was not calculated since the solid was quite hygroscopic and very little was recovered pure.

Anal. Calcd. for Co(NO₃)₃·6IV: C, 35.80; H, 4.51;

N, 3.48. Found: C, 34.85; H, 4.86; N, 3.73.

The acetone washings were added to the supernatant and the solution evaporated almost to dryness which produced a red oily material. The oil was transformed to a sticky solid by extracting with three 25 ml. portions of ether. The sticky solid was then recrystallized three times from acetone to give purple crystals which were filtered under nitrogen and dried under vacuum at room temperature. A yield was not calculated since the solid was quite hygroscopic and very little was recovered. The visible spectrum of the purple modification

indicated the cation to be $(Co \cdot 5IV)^+$ and the anion to be $Co(NO_3)_4^-$ (41).

Anal. Calcd. for $(Co \cdot 5IV)_2(Co \cdot 4NO_3)$: C, 35.55; H, 4.49; N, 2.77. Found: C, 35.22; H, 4.67; N, 2.92.

The Hydrolysis Product of IV (IVH_2O) and Coordination
Compounds of IVH_2O

$Zn(ClO_4)_2 \cdot 4(IVH_2O)$

To a stirred solution of 0.37 g. (1.0 mmole) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 10 ml. of acetone was added a solution of 1.28 g. (8.0 mmole) of IV in 10 ml. of acetone. There was an induction period of about 3 hr. before a colorless solid formed. The reaction mixture was allowed to stir for 2 hr. more after which the solid was filtered under nitrogen, washed with two 5 ml. portions of acetone, and dried under vacuum at room temperature. A total of 0.96 g. (98% yield) was collected. The complex is insoluble in acetone and ether and is soluble in ethanol, methanol and acetonitrile.

Anal. Calcd.: C, 29.48; H, 4.54; Cl, 7.26.

Found: C, 29.89; H, 4.75; Cl, 7.37.

$Cd(ClO_4)_2 \cdot 4(IVH_2O)$

To a stirred solution of 0.42 g. (1.0 mmole) of $Cd(ClO_4)_2 \cdot 6H_2O$ in 15 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 15 ml. of acetone. There was an induction period of about 8 hr. before a colorless solid formed. The reaction mixture was stirred for a total of 24

hr., after which the colorless solid was filtered under nitrogen, washed with two 5 ml. portions of acetone and two 5 ml. portions of ether, and dried under vacuum at room temperature. A total of 1.00 g. (98% yield) was collected. The solubility characteristics are the same as those reported for the zinc complex.

Anal. Calcd.: C, 28.10; H, 4.33; Cl, 6.92. Found:
C, 27.77; H, 4.20; Cl, 6.65.

$\text{Mn}(\text{ClO}_4)_2 \cdot 5(\text{IVH}_2\text{O}) \cdot \text{H}_2\text{O}$

To a stirred solution of 0.36 g. (1.0 mmole) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of acetone. A white solid formed after $1\frac{1}{2}$ hr. The reaction mixture was stirred for a total of 20 hr., after which the colorless solid was filtered under nitrogen, washed with two 5 ml. portions of acetone and two 5 ml. portions of ether, and dried under vacuum at room temperature. A 97% yield was realized. The solubility characteristics are the same as those reported for the zinc complex.

Anal. Calcd.: C, 31.00; H, 4.94; Cl, 6.10.
Found: C, 31.01; H, 4.90; Cl, 6.27.

$\text{Fe}(\text{ClO}_4)_2 \cdot 5(\text{IVH}_2\text{O}) \cdot \text{H}_2\text{O}$

To a stirred solution of 0.37 g (1.0 mmole) of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of acetone. A white solid formed after approximately 15 min. The reaction

mixture was stirred for 3 hr. after which the resulting colorless solid was filtered under nitrogen, washed with two 10 ml. portions of acetone and two 10 ml. portions of ether, and dried under vacuum at room temperature. The solubility properties are the same as those reported for the zinc complex. A 100% yield was realized.

Anal. Calcd.: C, 30.91; H, 4.93; Cl, 6.10.

Found: C, 30.88; H, 4.88; Cl, 5.90.

$\text{Nd}(\text{NO}_3)_3 \cdot 5(\text{IV H}_2\text{O}) \cdot \text{H}_2\text{O}$

To a stirred solution of 0.33 g. (0.76 mmole) of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 10 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 12 ml. of acetone. The reaction mixture was stirred for 13 hr. after which the resulting violet colored solid was filtered under nitrogen, washed with two 10 ml. portions of acetone and two 10 ml. portions of ether, and dried under vacuum at room temperature. A total of 0.80 g. (86% yield) was collected.

Anal. Calcd.: C, 29.10; H, 4.64; N, 3.39.

Found: C, 28.81; H, 4.71; N, 3.62.

Preparation of IVH_2O

To a stirred solution of 6.40 g. (40.0 mmole) of IV and 0.72 ml. (40.0 mmole) of H_2O in 20 ml. of acetone was added 1 drop of 70% HClO_4 . A colorless solid formed after 40 sec. The reaction mixture was stirred for 1 hr. and then the resulting solid was filtered under nitrogen, washed with two 5

ml. portions of acetone and two 5 ml. portions of ether, and dried under vacuum at room temperature. A second fraction of solid was collected by adding ether to the acetone supernatant. A total of 7.03 g. (99% yield) was collected.

Anal. Calcd.: C, 40.45; H, 6.24; P, 17.40.

Found: C, 40.62; H, 6.38; P, 17.40.

An investigation of infrared and nuclear magnetic resonance spectra of the solid revealed the presence of two isomers. The isomers were separated by fractional crystallization from absolute ethanol. The isomer that was the least soluble in ethanol, isomer A, was purified by recrystallization from boiling acetone. The more soluble isomer, isomer B, was purified by recrystallization from methanol.

Uncharacterized Complexes of IV

NiCl₂ + IV

Anhydrous NiCl₂ was obtained by drying NiCl₂·6H₂O in an oven at 120° for 12 hr. (41). To a solution of 0.13 g. (1.0 mmole) of NiCl₂ in 30 ml. of dry absolute ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of absolute ethanol. A reaction took place since a color change was noted, but no solid formed. A rust colored solid was obtained by adding an equal volume of ether to the solution. The solid was filtered under nitrogen and dried under vacuum at room temperature. A total of 1.09 g. was collected which would be a 100% yield based on a six coordinate complex. The complex

was purified by repeatedly dissolving in methanol and flooding out with ether. The infrared spectrum showed IV to be present, however, no conclusion concerning stoichiometry could be derived from the elemental analyses.

CoCl₂ + IV

Anhydrous CoCl₂ was prepared in the same manner as reported for NiCl₂. To a solution of 0.13 g. (1.0 mmole) of CoCl₂ in 15 ml. of acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of acetone. A blue solid formed immediately which turned to a green solid upon standing. The solid was filtered under nitrogen, washed with acetone and dried under vacuum at room temperature. A total of 0.85 g. was collected. The solid gives a yellow solution in water and methanol which might indicate the presence of Co(IV)₅⁺. The complex was purified by recrystallization from absolute ethanol. The infrared spectrum showed IV to be present. The elemental analyses were poor for all reasonable formulations.

CuCl₂ + IV

Anhydrous CuCl₂ was prepared in the same manner as reported for NiCl₂. To a stirred solution of 0.13 g. (1.0 mmole) of CuCl₂ in 40 ml. of boiling acetone was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of acetone. The color of the solution went from yellow-brown to red-orange, and cooling to 0° for 12 hr. resulted in a light yellow solid under a light yellow supernatant. Recrystallization of the complex from methanol gave colorless crystals. However, no

conclusions concerning stoichiometry could be derived from the elemental analyses.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{IV}$

To a stirred solution of 0.25 g. (1.0 mmole) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 80 ml. of boiling ethanol was added a solution of 1.60 g. (10.0 mmole) of IV in 10 ml. of boiling ethanol. The blue color of the solution disappeared and a colorless solid formed after 12 hr. The elemental analyses gave no clue as to the identity of the complex.

$\text{PtCl}_2 \cdot 4\text{py} + \text{IV}$

The starting material, $\text{PtCl}_2 \cdot 4\text{py}$, was prepared by a method reported elsewhere (40). To a stirred solution of 0.58 g. (1.0 mmole) of $\text{PtCl}_2 \cdot 4\text{py}$ in 20 ml. of methanol was added a solution of 1.60 g. (10.0 mmole) of IV in 20 ml. of methanol. The solution was stirred for 30 min., evaporated to dryness, and the excess ligand removed by sublimation. The crude complex was purified by repeatedly dissolving in ethanol and precipitating the compound by addition of ether to the solution. The complex was ionic as shown by its molar conductivity and the weight of the complex obtained was commensurate with a 90% yield based on $\text{PtCl}_2 \cdot 4\text{IV}$. However, the infrared spectrum showed an absorption in the OH region and the elemental analyses did not correspond to any reasonable formulations.

Coordination Compounds of Open-Chain Trialkyl Phosphites
 $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{P}(\text{OEt})_3$

To a stirred solution of 0.74 g. (2.0 mmole) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10 ml. of acetone was added 3.44 ml. (20.0 mmole) of $\text{P}(\text{OEt})_3$. There was an immediate color change from green to red-orange, and the addition of an equal volume of ether resulted in an orange-yellow solid. The solid was filtered under nitrogen, washed with four 5 ml. portions of ether, and dried under vacuum at room temperature. A total of 2.00 g. (90% yield) was collected.

Anal. Calcd.: Ni, 4.68; C, 34.45; H, 7.23; Cl, 5.65.

Found: Ni, 4.68; C, 34.39; H, 7.28; Cl, 6.03.

$\text{Ni}(\text{ClO}_4)_2 \cdot 5\text{P}(\text{OMe})_3$

To a stirred solution of 0.37 g. (1.0 mmole) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 10 ml. of acetone was added 0.99 g. (8.0 mmole) of $\text{P}(\text{OMe})_3$. There was an immediate color change from green to red-orange. The solution was stirred for 1 hr. and then an equal volume of ether was added producing a yellow-orange solid. The somewhat sticky solid was extracted with two 5 ml. portions of ether, and then purified by repeatedly precipitating the compound from an acetone solution by adding ether. The solid was dried under vacuum at room temperature. An 80% yield was realized.

Anal. Calcd.: Ni, 6.69; C, 20.52; H, 5.17; Cl, 8.07.

Found: Ni, 6.64; C, 19.84; H, 5.08; Cl, 8.03.

$\text{Cu}(\text{ClO}_4) \cdot 4\text{P}(\text{OMe})_3$

To a stirred solution of 0.74 g. (2.0 mmole) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 15 ml. of acetone was added 2.48 g. (20.0 mmole) of trimethyl phosphite. Then 0.28 g. (2.0 mmole) of K_2CO_3 was immediately added to neutralize the perchloric acid generated in this reaction. The reaction mixture was stirred for 30 min., the KClO_4 which formed was filtered and a large excess of anhydrous ether was added to the supernatant producing a colorless solid. The solid was filtered under nitrogen, washed with three 5 ml. portions of ether, and dried under vacuum at room temperature. An 87% yield was realized.

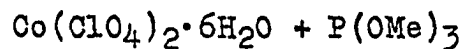
Anal. Calcd.: C, 21.85; H, 5.50; Cl, 5.38.

Found: C, 22.15; H, 5.63; Cl, 5.60.

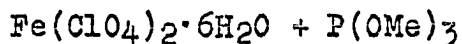
Uncharacterized Complexes and Attempted

Preparations of Open-Chain Trialkyl Phosphites

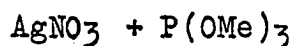
The general method of preparation involved adding the trialkyl phosphite in a 10:1 mole ratio to a stirred solution of the desired metal salt in acetone or ethanol. The reaction mixture was stirred for a definite period of time, and then an equal volume of ether was added to produce the solid complex or an oil. The solid was filtered under nitrogen, washed several times with ether, and dried under vacuum at room temperature.



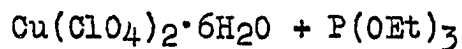
There was an immediate reaction as noted by a color change from violet to dark brown. The addition of ether to the acetone solution resulted in the formation of an oil which solidified after washing several times with ether. The crude solid was then extracted with a small quantity of acetone. A small amount of undissolved yellow solid remained which was insufficient for analysis.



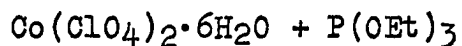
There was an immediate reaction as noted by the formation of a finely-divided solid. After the reaction mixture was stirred for 4 hr., an equal volume of ether was added to the acetone solution producing a sticky solid which was washed several times with ether and extracted with acetone. The resulting tan-colored solid was filtered under nitrogen, washed with ether and dried under vacuum at room temperature. The solid was not characterized.



Only an intractable oil was isolated from the ethanol solution.

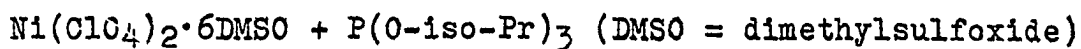


The acetone solution went from blue to colorless immediately, but no solid could be obtained upon adding ether.

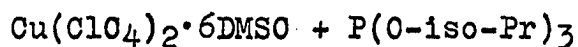


There was an immediate color change in the acetone solution from violet to dark brown, and a small amount of yellow-

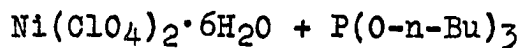
orange solid was obtained upon the addition of ether. The solid was not characterized.



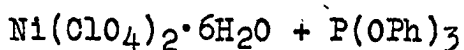
There was an immediate reaction in the acetone solution as noted by color change, but no solid could be recovered except unreacted starting material.



There was no apparent reaction in the acetone solution and only unreacted starting material was recovered.



The acetone solution changed in color from green to red-orange, but no solid could be obtained by the addition of an equal volume of ether.



There was an immediate reaction in the acetone solution as noted by color change, but only an intractable oil was recovered.



The acetone solution turned red in color after stirring for 12 hr., and a red-brown sticky solid was produced upon the addition of ether. The supernatant was decanted from the crude solid and a small quantity of acetone was added with the result that a red supernatant over some red-brown crystals was produced. The solid was not characterized.

Physical Measurements

Cobalt analysis

Samples ranging from 10-15 mg. were decomposed by evaporating almost to dryness with two 3 ml. portions of concentrated HNO_3 and then with two 3 ml. portions of 70% HClO_4 to insure complete decomposition. The divalent cobalt ion was then converted to the chloride by evaporation with 1 ml. of HCl , and the residue analyzed for cobalt spectrophotometrically according to the method of Pepkowitz and Marley (42). Hexaamminecobalt(III) chloride was used as a standard.

Nickel analysis

Nickel analyses were carried out by slowly decomposing 200 to 225 mg. samples suspended in 15 ml. of water with 5 ml. of concentrated HNO_3 and evaporating nearly to dryness on a steam bath. The evaporation was repeated with 5 ml. of 70% HClO_4 followed by dilution to about 100 ml. with water. The nickel content was then determined by a standard gravimetric procedure (43) as the dimethylglyoxime complex.

Silver analysis

The samples were decomposed in the same manner as the nickel samples, and the silver content determined by a standard titrimetric procedure (44) using a standardized KCNS solution.

Copper analysis

The samples were decomposed in the same manner as the nickel samples, and the copper content determined iodometrically (45) by a standard titration procedure.

Phosphorus analysis

Phosphorus analyses were carried out by the Schoniger procedure (46) in which the compound is burned forming P_2O_5 which is absorbed into an alkaline hypobromite solution and precipitated with quinoline molybdate reagent. The phosphorus content was then determined by adding excess base to the precipitated quinolinium phosphomolybdate and backtitrating with acid. It was found necessary to digest the precipitate overnight to obtain consistent results.

Nuclear magnetic resonance spectra

The proton chemical shifts and coupling constants for IV and its derivatives are summarized in Table 2, and the proton resonance spectra of adamantane-like molecules are shown in Figure 2. All peaks are measured in p.p.m. downfield with respect to tetramethylsilane and coupling constants are given in c.p.s.

The proton chemical shifts (in p.p.m. downfield with respect to tetramethylsilane) and coupling constants (c.p.s.) for n.m.r. spectra of $Cd(ClO_4)_2 \cdot 4IVH_2O$, and isomer A and isomer B of IVH_2O in D_2O solution are summarized in Table 3. Pertinent n.m.r. spectra are shown in Figure 3.

Table 2. N.m.r. spectra of IV and its derivatives

Compound	Solvent	H _{ax}	H _{eq}	H _{methine}	J _{HOH}	J _{POCH}
IV	(CH ₃) ₂ SO	1.95	2.90	4.28	14.0	6.3 ^a
IV-oxide	CD ₃ CN	1.90	2.56	5.00	14.0	20.0
IV-sulfide	(CH ₃) ₂ SO	1.85	2.73	4.97	14.0	19.0
IV·BH ₃ ^b	CD ₃ CN	2.05	2.85	4.88	14.0	12.5
IV·B(CH ₃) ₃ ^b	CD ₃ CN	1.98	2.87	4.38	14.0	6.7
IV·BF ₃ ^b	CD ₃ CN	1.97	2.87	4.33	14.0	--
(IV·CH ₂ CH ₃) ⁺ BF ₄ ⁻	CD ₃ CN	2.33	3.08	5.37	15.0	15.7
(IV·CPh ₃) ⁺ BF ₄ ⁻	CD ₃ CN	2.34	3.18	5.45	16.0	18.0
(IV·CPh ₃) ⁺ ClO ₄ ⁻	CD ₃ CN	2.34	3.18	5.45	16.0	18.0
Co(ClO ₄)·5IV	D ₂ O	1.95	2.88	4.90	15.0	--
Co(ClO ₄) ₃ ·6IV	CD ₃ CN	2.14	3.05	4.97	15.2	--
Ni(ClO ₄) ₂ ·5IV·H ₂ O	D ₂ O	2.21	3.08	4.97	15.0	--
Ni(ClO ₄) ₂ ·6IV	D ₂ O	2.21	3.05	4.93	15.8	--
Cu(NO ₃)·4IV	D ₂ O	2.09	3.03	4.64	14.3	--
Ag(NO ₃)·4IV	CH ₃ CN	--	2.96	4.48	13.3	10.0

^aThis value was obtained from the P-31 n.m.r. spectrum of IV.

^bSee reference 27.

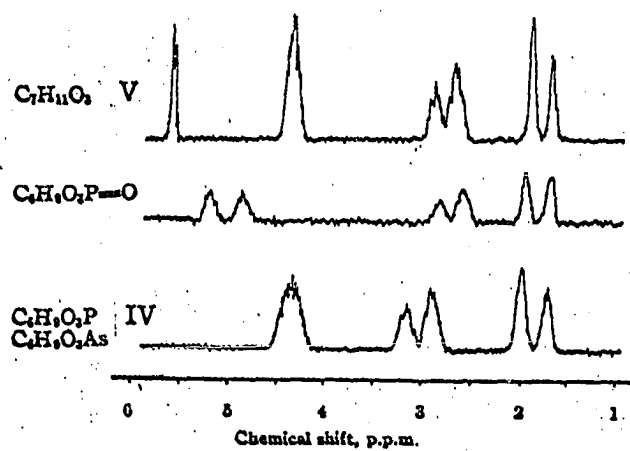


Figure 2. ^1H resonance spectra of adamantane-like molecules in CDCl_3 solution. All peaks downfield with respect to tetramethylsilane

Figure 3. H^1 resonance spectra of $Cd(ClO_4)_2 \cdot 4IVH_2O$, and isomer A and isomer B of IVH_2O in D_2O solution. All peaks downfield with respect to tetramethylsilane

42b

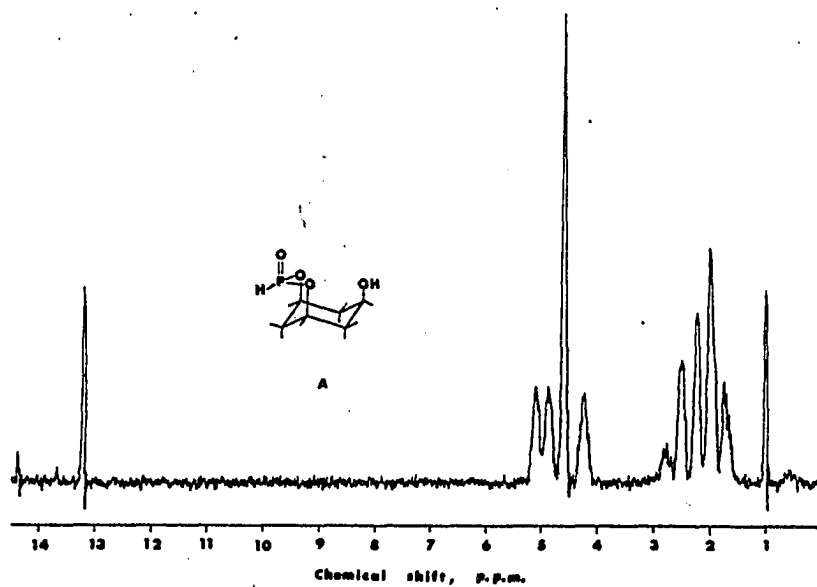
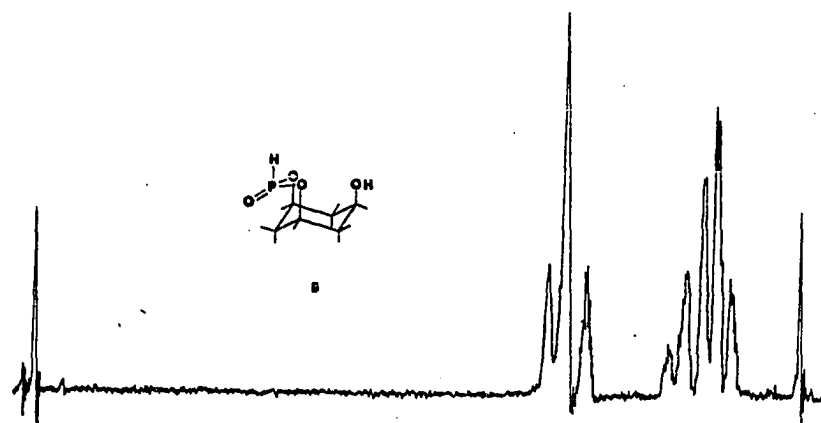
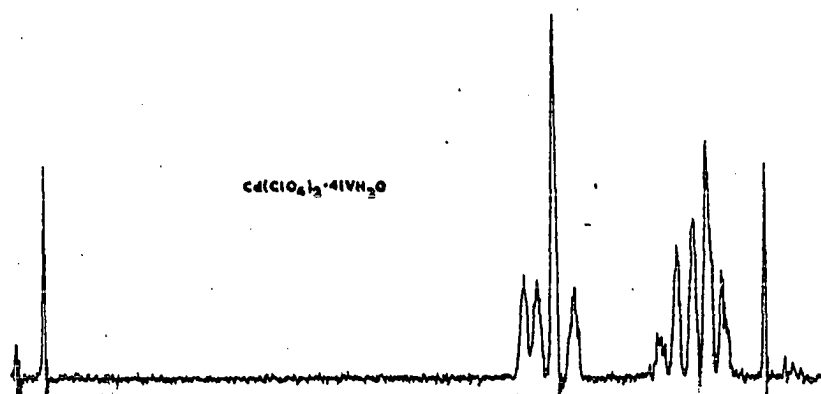


Table 3. N.m.r. spectra of $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{IVH}_2\text{O}$ and isomer A and isomer B of IVH_2O

Compound	H_{ax}	H_{eq}	$H(\text{HOCH})$	H_{CH}	H_{PH}	J_{HCH}	J_{POCH}	J_{PH}
Isomer A	1.98	2.46	4.32	5.06	7.20	15	13	730
Isomer B	2.00	2.48	4.30	4.84	7.17	15	14	781
$\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{IVH}_2\text{O}$	1.94	2.44	4.31	5.05	7.21	17	13	735

Infrared spectra

The important infrared bands of IV and its derivatives are summarized in Table 4, and those of the complexes of IVH_2O and isomer A and isomer B of IVH_2O are reported in Table 5. Infrared spectra of those compounds containing ionic perchlorate or nitrate anions exhibited bands readily assignable to these ions (47).

Visible and ultraviolet spectra

The observed bands in the electronic absorption spectra of the complexes of IV are summarized in Table 6.

Molar conductivities

The molar conductivities of the complexes and phosphonium salts of IV are presented in Table 7. The conductances agree quite well with the standards used. The two-ion standard, tetra-n-butylammonium nitrate, was prepared by treating an aqueous solution of the corresponding bromide with a calculated amount of AgNO_3 . The tetra-n-butylammonium bromide was prepared by a method reported elsewhere (48). The two ion

Table 4. Infrared spectra of IV and its derivatives^a

Compound	Frequency in cm. ⁻¹			
	O-H bands	C-H stretch	P-O-C stretch	B-P stretch
IV	-	2970	1040	
IV=oxide ^b	-	2970	1037	
IV-sulfide	-	2980	1037	
IV·BH ₃ ^c	-	-	1035	860
IV·B(CH ₃) ₃ ^c	-	-	1030	833
IV·BF ₃ ^c	-	-	1030	854
(IV·CH ₂ CH ₃) ⁺ BF ₄ ⁻	-	3000	1031	
(IV·CPh ₃) ⁺ BF ₄ ⁻	-	3000	1031	
(IV·CPh ₃) ⁺ ClO ₄ ⁻	-	3000	1031	
CuClO ₄ ·4IV	-	2950	1038	
CuNO ₃ ·4IV	-	2980	1035	
AgClO ₄ ·4IV	-	2980	1038	
AgNO ₃ ·4IV	-	2980	1038	
AuCl·IV	-	2950	1031	
Ni(ClO ₄) ₂ ·6IV	-	2980	1031	
Ni(ClO ₄) ₂ ·5IV·H ₂ O	3510, 1625	2970	1033	
Ni(NO ₃) ₂ ·5IV·H ₂ O	3510, 1625	2980	1032	
Ni·4IV	-	2970	1032	
PtCl ₂ ·2IV	-	2970	1029	
CoClO ₄ ·5IV	-	2970	1032	
Co(ClO ₄) ₃ ·6IV	-	2970	1032	
(Co·5IV) ₂ (Co·4NO ₃)	-	2970	1031	

^aAll bands were of medium intensity.^bThe P=O stretch occurs at 1308 cm.⁻¹.^cSee reference 25.

Table 5. Infrared spectra of complexes of IV H₂O and isomer A and isomer B

Compound	Frequency in cm ⁻¹				
	O-H (m)	C-H (m)	P-H (w)	P=O (s)	P-O-C (m)
Isomer A	3450	2940	2440	1241	976
Isomer B	3440	2940	2510	1209	981
Zn(ClO ₄) ₂ ·4(IV H ₂ O)	3400	2900	2450	1209	977
Od(ClO ₄) ₂ ·4(IV H ₂ O)	3400	2940	2440	1228	977
Mn(ClO ₄) ₂ ·5(IV H ₂ O)·H ₂ O	3550 3380 1620	2930	2460	1222	976
Fe(ClO ₄) ₂ ·5(IV H ₂ O)·H ₂ O	3560 3440 1620	2940	2440	1227	973
Nd(NO ₃) ₃ ·5(IV H ₂ O)·H ₂ O	3520 3400 1625	2920	2460	1210	980
<p>s = strong</p> <p>m = medium</p> <p>w = weak</p>					

Table 6. Electronic absorption spectra of complexes of IV

Compound	Solvent	λ (m μ) ^a
Co(ClO ₄) · 5IV	H ₂ O	230 ^b (1.5x10 ⁴), 342(1.4x10 ³)
Co(ClO ₄) ₃ · 6IV ^c	H ₂ O	232(5.0x10 ⁴), 265(1.1x10 ⁴), 298(2.0x10 ³) 320(337)
Ni(ClO ₄) ₂ · 6IV	CH ₂ Cl ₂	365(3.5x10 ³)
Ni(ClO ₄) ₂ · 5IV · H ₂ O	H ₂ O	350(2.7x10 ³)
Ni · 4IV	CH ₃ ON	222(2.7x10 ⁴)

^aExtinction coefficients appear in parentheses.

^bAppears as a shoulder on the ultraviolet tail.

^cThe bands reported for this compound were resolved by Gaussian analysis.

Table 7. Molar conductances of transition metal complexes and phosphonium salts of IV

Complex	Molar conductance (mhos/cm. mole)	
	Water	Acetonitrile
$\text{AgNO}_3 \cdot 4\text{IV}$	104	147
$\text{AgClO}_4 \cdot 4\text{IV}$	-	160
$\text{CuNO}_3 \cdot 4\text{IV}$	91	-
$\text{CuClO}_4 \cdot 4\text{IV}$	86	150
$\text{CoClO}_4 \cdot 5\text{IV}$	80	135
$(n\text{-C}_4\text{H}_9)_4\text{NNO}_3$	85	158
$\text{Ni}(\text{ClO}_4)_2 \cdot 5\text{IV} \cdot \text{H}_2\text{O}$	241	285
$\text{Ni}(\text{NO}_3)_2 \cdot 5\text{IV} \cdot \text{H}_2\text{O}$	238	-
$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{IV}$	-	320
$\text{Ni}(\text{ClO}_4)_2 \cdot 3\text{en}$	253	312
$\text{Co}(\text{ClO}_4)_3 \cdot 6\text{IV}$	333	-
$\text{Co}(\text{NO}_3)_3 \cdot 3\text{en}$	389	-
$\text{Co}(\text{ClO}_4)_3 \cdot 3\text{en}$	376	-
$\text{Ni} \cdot 4\text{IV}$	-	3
$\text{AuCl} \cdot \text{IV}$	-	3
$(\text{IV} \cdot \text{CPh}_3)^+ \text{ClO}_4^-$	-	132
$(\text{IV} \cdot \text{CPh}_3)^+ \text{BF}_4^-$	-	155
$(\text{IV} \cdot \text{CH}_2\text{CH}_3)^+ \text{BF}_4^-$	-	151

standard, tris-ethylenediamminenickel(II) perchlorate, and the three ion standard, tris-ethylenediamminecobalt(III) perchlorate, were prepared by treating the corresponding halides with a calculated amount of AgClO_4 and recrystallizing the resulting solids from 50% ethanol. The halides were synthesized by standard methods (49,50).

Dipole moments

The orientation polarization and dipole moments of some of the compounds reported in this investigation are listed in Table 8. Mole fractions were in the range 0.002 to 0.020.

Table 8. Dipole moment data for compounds at $25.00 \pm 0.05^\circ\text{C}$

Compound	Mol. wt.	Solvent	$\frac{dn}{dx}$	$\frac{d\epsilon}{dx}$	P_0	(Debyes) ^a
$\text{C}_6\text{H}_9\text{O}_3\text{P}$ (IV)	160.11	dioxane	0.146	29.17	416	4.51
$\text{C}_6\text{H}_9\text{O}_3\text{P}$ (IV)	160.11	CHCl_3	0.148	59.16	317	3.94
$\text{C}_6\text{H}_9\text{O}_3\text{P}=\text{O}$	176.11	CHCl_3	---	161.96	867	6.51
$\text{C}_6\text{H}_9\text{O}_3\text{P}=\text{S}$	192.17	CHCl_3	0.137	151.65	810	6.30
$\text{C}_6\text{H}_9\text{O}_3\text{As}$	204.06	dioxane	---	10.28	145	2.66
$\text{C}_6\text{H}_9\text{O}_3\text{CH}$	142.16	dioxane	---	15.68	228	3.34
$(\text{C}_2\text{H}_5\text{O})_3\text{P}^b$	166.16	dioxane	---	---	110	1.82

^aMaximum error in all cases was no more than $\pm 0.05\text{D}$.

^bSee reference 37.

According to Buckingham (50) polar groups in a molecule will generate an electric field and affect the electronic environment about other nuclei in the molecule, and can lead to chemical shifts that are proportional to the power of the field strength. The change in the proton screening constant, $\Delta \sigma$, is approximately given by $\Delta \sigma = -2 \times 10^{-12} E_z - 10^{-18} E^2$, where E is the electric field generated and E_z is the component of E in the bond direction. The proton resonance will occur at lower magnetic field strengths if the electric field is directed along the X-H direction and at a higher magnetic field strength if it is in the H-X direction. Highly polar neighboring solvent molecules will also generate an electric field and may lead to a solvent shift related to the dielectric constant of the solvent. Such solvent effects were not considered in this model. The quantities E and E_z are calculated using the formulas

$$E = E_r + E_\theta = \text{electric field at the proton}$$

$$E_z = E_r \cos \theta_1 + E_\theta \cos \theta_2 = \text{component of } E \text{ in the bond direction.}$$

According to Peck (51) E_r and E_θ are given by:

$$E_r = 2\mu \cos \theta / r^3 \text{ and } E_\theta = \mu \sin \theta / r^3.$$

Figure 4 contains the relevant vector and sign conventions.

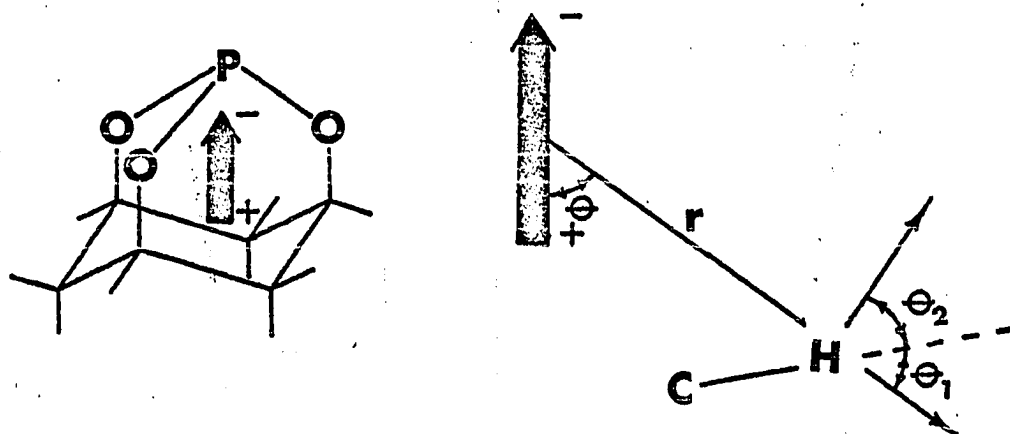


Figure 4. Point dipole representation

The measured value of the dipole moment of IV in dioxane, 4.51 D., was used. In order to determine the location of the threefold axis in IV, the perpendicular distance from every carbon atom in the cyclohexane part of IV was mathematically calculated from geometrical considerations and accepted bond distances to be 1.44 \AA . The measured value of the chemical shift of the methylene protons in the parent molecule of IV, adamantane, was -1.77 p.p.m. in CCl_4 . The chemical shifts in cyclohexane of the methylene protons in IV were arbitrarily assigned as $H_{eq} = -2.95$ and $H_{ax} = -1.84 \text{ p.p.m.}$ It can be seen from the previous formulas that if the model used is correct then $\Delta\sigma_{eq} = -1.18$ and $\Delta\sigma_{ax} = -0.07 \text{ p.p.m.}$ The values for θ , r , θ_1 and θ_2 were then determined graphically as shown in Figure 5. The results of the points tried are shown in Table 9, and a plot of $\Delta\sigma$ vs. (distance up the

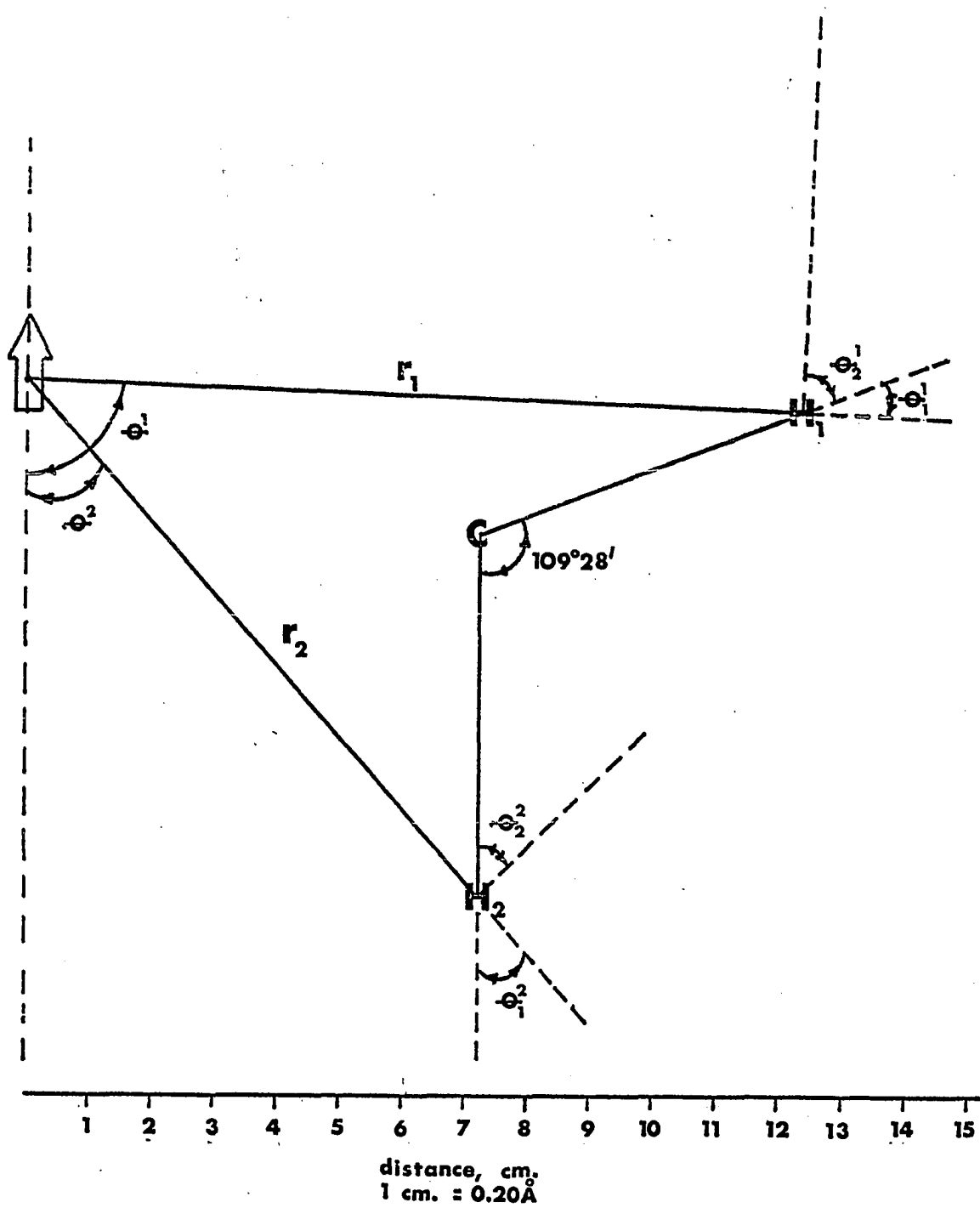


Figure 5. Determination of θ , r , θ_1 and θ_2

threefold axis from the plane of carbon atoms under consideration) is shown in Figure 6.

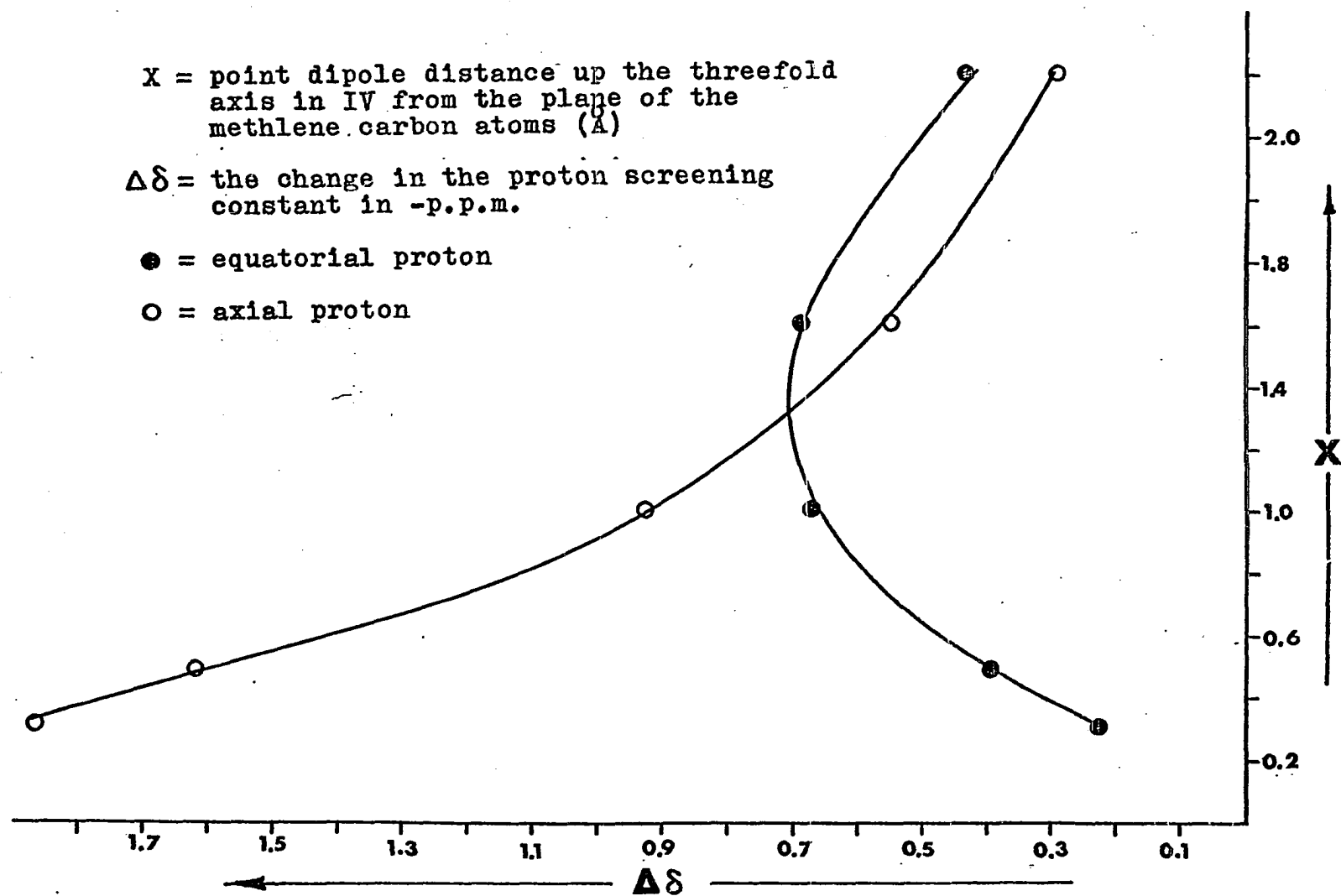
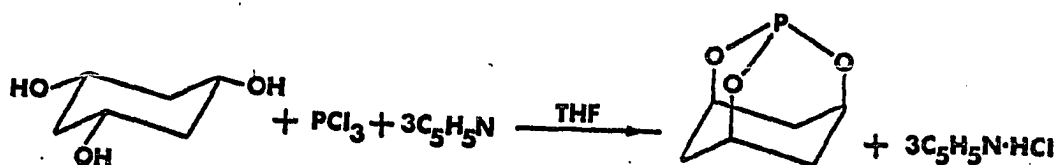


Figure 6. Point dipole determination of H_{eq} and H_{ax}

DISCUSSION

2,8,9-Trioxa-1-phospha-adamantane (IV)

It is significant that IV is obtained in a much higher yield (90%) when the preparation is carried out via an ester exchange than when PCl_3 is used as the starting material (29). In the preparation herein described, effects due to



solvent interaction as well as possible interaction with base and halide ion are eliminated, thus reducing the probability of polymer formation. The rigidity and high symmetry of the constrained phosphite ester undoubtedly contribute to its resistance to air oxidation as well as to its ease of sublimation. The phosphate and thiophosphate derivatives of IV are also stable toward air or water.

A scale model of IV shows the tricyclic phosphite to be a rigid but essentially strainless caged structure. The relatively high melting point of IV (208°), as well as of its phosphate and thiophosphate derivatives (275° and 250° , respectively) is an indication of a high lattice energy for these solids. Dipole-dipole interactions are also undoubtedly a main contributing factor to the lattice energy of the

solid. It is significant that IV and the phosphate and thiophosphate derivatives of IV have large dipole moments (3.94, 6.51 and 6.30 D., respectively in chloroform). The relatively low solubility of IV in non-polar or slightly polar solvents compared to other polycyclic phosphites (26) is also in line with a high lattice energy.

The caged phosphite has been shown to be a good Lewis base in a study of its 1:1 adducts with the Lewis acids BH_3 , B_3H_7 , $\text{B}(\text{CH}_3)_3$ and BF_3 (25). A comparison of the 1:1 adducts formed between trimethyl phosphite and borane, III and borane, and IV and borane shows IV to be the strongest Lewis base. This is undoubtedly a result of the higher dipole moment of IV as well as the difference in electronic environment about the two phosphorus nuclei. However, P^{31} n.m.r. has revealed that the phosphorus nucleus in IV and in trimethyl phosphite is shielded to about the same extent (27), thus indicating that the difference in the base strengths is perhaps mainly a dipole effect. The fairly strong basicity of IV is also indicated in its reaction with $(\text{H}_3\text{C})_3\text{NBH}_3$, in which IV displaces the $(\text{H}_3\text{C})_3\text{N}$ (26).

The assignment of the proton chemical shifts in the n.m.r. spectrum of IV is not obvious from models. The peak which occurs farthest downfield at -4.24 p.p.m. is easily assigned to the methine proton as it is most strongly affected by the highly electronegative oxygen atom. The H^1 n.m.r. spectrum in Figure 7 reveals two doublets at -1.93 and

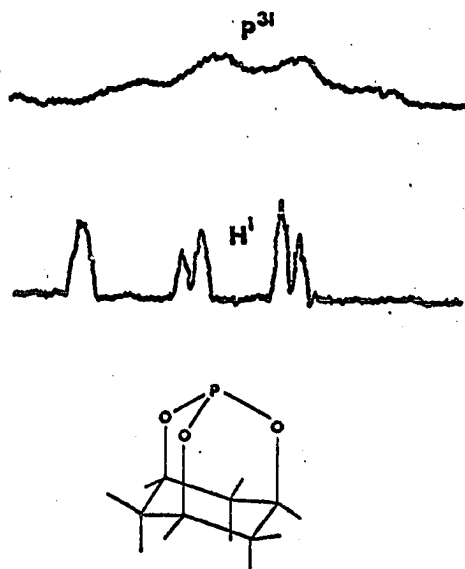


Figure 7. H^1 and P^{31} resonance spectra of IV in CDCl_3 solution. All peaks downfield with respect to tetramethylsilane

-2.90 p.p.m. arising from spin-spin coupling between the two chemically different axial and equatorial methylene protons. The assignment of these doublet absorptions will now be discussed.

Effects which may play an important role in determining the chemical shifts of the methylene protons are (a) molecular dipole, (b) solvation, and (c) polarity of the solvent used in the measurement. Much might also be derived from a knowledge of the chemical shifts of structurally similar molecules.

If a partial charge separation is assumed to occur within the adamantane molecule, IV, then to a fair approximation the partial negative charge resides in the PO_3 moiety and the partial positive charge in the cyclohexane ring portion of the molecule. A distribution of this positive charge places a larger portion of it on the methinyl carbons due to the inductive effect of the electronegative oxygen atoms. The net result is a deshielding of the methinyl and methylene protons, the methinyl protons being deshielded to a greater extent than the equally deshielded methylene protons. Hence, this model gives no information as to which proton, H_{ax} or H_{eq} , is shifted farthest downfield.

However, if a point dipole model is considered, the relative chemical shifts of H_{ax} and H_{eq} can be predicted. A point dipole is assumed to lie along the threefold axis of IV. The angle which each C-H bond makes with respect to this

axis should serve to differentiate the protons under consideration (30). By placing points on the threefold axis and mathematically determining the effect of the axial and equatorial protons from each of these points, it was concluded (see Table 9) that H_{ax} should be shifted downfield from H_{eq} since the C- H_{ax} bond axis is almost parallel to the electric field created by the dipole, and is thus affected to the greatest extent (52).

The effect of solvation on chemical shifts can be incorporated using a model discussed by Buckingham (30). The expected orientation of the nearest neighbor solvent molecules around the solute molecule would direct the negative ends of their dipoles toward the cyclohexane portion of IV, as depicted in Figure 8. The resulting "reaction field" ($E + E_z$) produced by the solvent molecules would strengthen any molecular dipole effect which might be operative.

A consideration of the effect of increasing the polarity of the solvent on the chemical shifts of the methylene protons in adamantane systems indicates that the equatorial protons should be downfield with respect to the axial protons. A "reaction field" which increases with the dielectric constant of the solvent is produced by the solvent molecules around the solute (30). The direction of this field is in the opposite sense to that of the solute dipole and produces a larger potential gradient on the C-H bonds lying between

Table 9. Data on point dipole calculations

Distance up axis (\AA)	Position	θ	$r(\text{\AA})$	θ_1	θ_2	$E_r(\times 10^{-6})$	$E_\theta(\times 10^{-6})$
0.300	eq	$91^\circ 40'$	2.48	18°	72°	-0.0172	0.2960
	ax	46°	2.01	46°	136°	0.7720	0.4000
0.480	eq	$87^\circ 20'$	2.48	22°	68°	0.0275	0.2960
	ax	$42^\circ 10'$	2.13	$42^\circ 10'$	$47^\circ 50'$	0.6930	0.3139
1.00	eq	$75^\circ 50'$	2.55	34°	56°	0.1337	0.2645
	ax	35°	2.54	35°	125°	0.4510	0.1580
1.60	eq	$63^\circ 40'$	2.76	46°	44°	0.1908	0.1929
	ax	$28^\circ 10'$	3.05	$28^\circ 10'$	$118^\circ 10'$	0.2805	0.0754
2.40	eq	$50^\circ 30'$	3.21	59°	31°	0.1734	0.1054
	ax	$22^\circ 20'$	3.78	$22^\circ 20'$	$112^\circ 20'$	0.1547	0.0318

Table 9. (continued)

Distance up axis (\AA)	Position	$E(\times 10^{-6})$	$E_z(\times 10^{-6})$	$\Delta\delta_{eq.}(\text{ppm})$	$\Delta\delta_{ax.}(\text{ppm})$
0.300	eq	0.2788	0.0751	-0.2280	---
	ax	1.1720	0.2481	---	-1.8652
0.480	eq	0.3235	0.1466	-0.3978	---
	ax	1.0069	0.3030	---	-1.616
1.00	eq	0.3982	0.2588	-0.6760	---
	ax	0.6090	0.2784	---	-0.9278
1.60	eq	0.3837	0.2712	-0.6899	---
	ax	0.3559	0.2119	---	-0.5505
2.40	eq	0.2793	0.1799	-0.4376	---
	ax	0.1865	0.1309	---	-0.2967

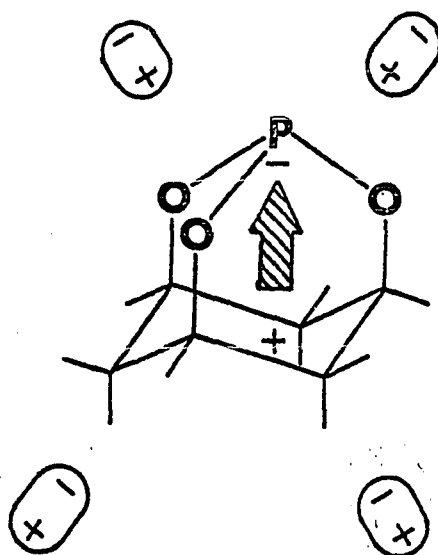


Figure 8. Solvent interactions with polar solute molecules such as IV

the molecular and solvent dipoles. The net effect is a downfield shift of H_{ax} and a small upfield shift of H_{eq} when the dielectric constant of the solvent is increased. The change in chemical shift of the protons on $C_6H_9O_3P$ (IV), $C_7H_{10}O_3$ (V), and $C_6H_9O_3As$ with an increase in the polarity of the solvent is shown in Table 10. Although the change is small, the H_{eq} peak should appear downfield with respect to the H_{ax} peak.

A comparison with other substituted cyclohexanes and acetylated sugars (see Figure 9) indicated that the axial methylene protons in IV and its analogues should appear at higher field than the equatorial (53). The n.m.r. spectrum of the orthoformate of IV, shown in Figure 2, reveals much unresolved fine splitting in the doublet at low field. A Dreiding model shows a slight strain in the cage resulting in the equatorial protons and the methine protons being almost coplanar. It has been shown by Karplus (54) that the coupling between two protons is greatest when they are coplanar. This would explain the fine splitting in the downfield doublet and would therefore support the assignment of this absorption to the equatorial proton.

The predictions of the dipole and solvation effects on the chemical shifts of the axial and equatorial protons contradict those due to solvent polarity changes as well as those found in similar molecules such as acetylated sugars and substituted cyclohexanes. It is the author's belief that the theoretical models based on dipole and solvation effects

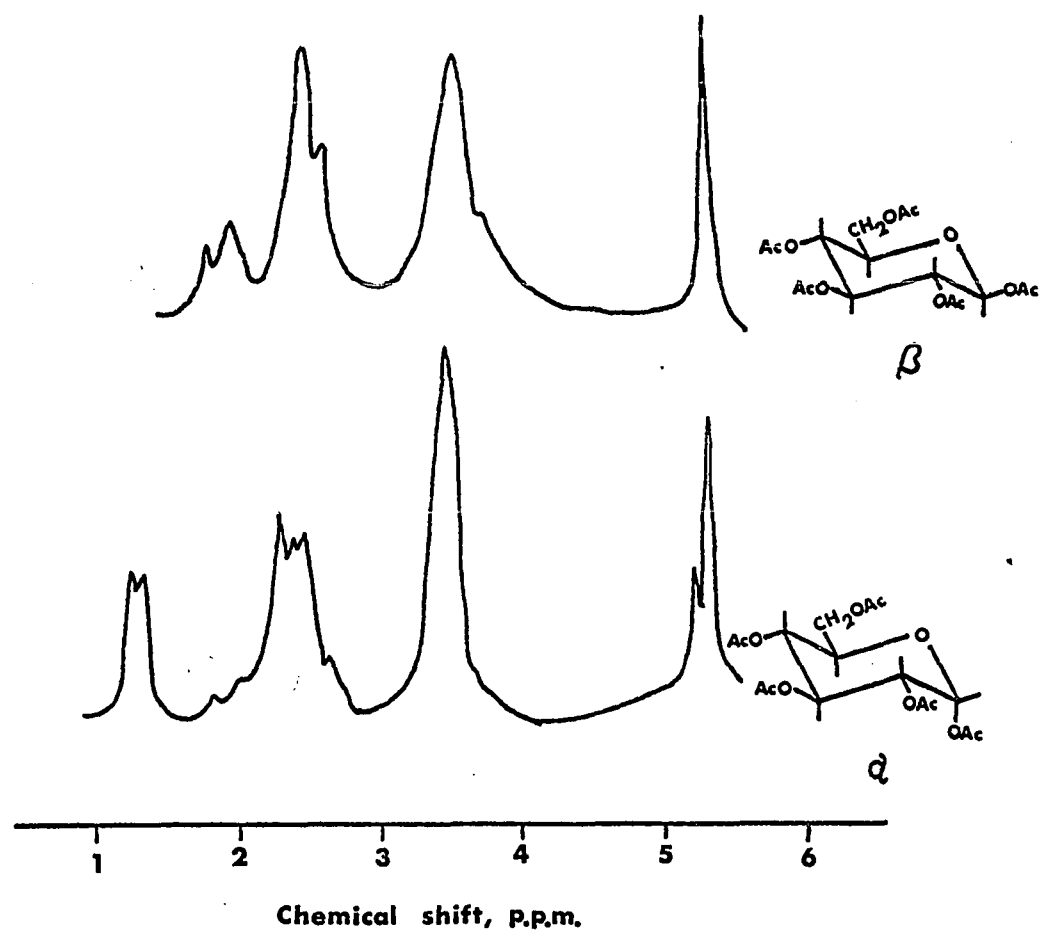


Figure 9. H^1 resonance spectra of α - and β -D-glucopyranose in CHCl_3 solution. All peaks upfield with respect to CHCl_3

Table 10. Proton chemical shifts (-p.p.m. vs. $\text{Si}(\text{CH}_3)_4$) at infinite dilution in solvents of decreasing dielectric constant

Compound	Solvent	H_{ax}	H_{eq}	H_{methinyl}
$\text{C}_6\text{H}_9\text{O}_3\text{P}$ (IV)	DMSO^{a}	1.95	2.90	4.28
	CD_3CN	1.93	2.90	4.24
	$(\text{CH}_3)_2\text{CO}$	---- ^b	2.92	4.30
	CH_2Cl_2	1.90	2.98	4.30
	CDCl_3	1.89	3.04	4.34
	CCl_4	1.82	2.99	4.20
	C_6H_{12}	1.84	2.95	4.15
$\text{C}_6\text{H}_9\text{O}_3\text{As}$	DMSO^{a}	1.94	---- ^b	4.26
	CD_3CN	1.95	2.94	4.23
	$(\text{CH}_3)_2\text{CO}$	---- ^b	2.93	4.27
	CH_2Cl_2	1.89	3.05	4.28
	CDCl_3	1.88	3.10	4.36
	CCl_4	1.79	3.02	4.24
	C_6H_{12}	---- ^b	2.99	4.14
$\text{C}_7\text{H}_{10}\text{O}_3$ (V)	DMSO^{a}	1.80	---- ^b	4.25
	CD_3CN	1.79	2.55	4.23
	$(\text{CH}_3)_2\text{CO}$	---- ^b	2.59	4.27
	CH_2Cl_2	1.73	2.66	4.28
	CDCl_3	1.78	2.77	4.36
	CCl_4	1.65	2.65	4.24
	C_6H_{12}	---- ^b	---- ^b	4.14

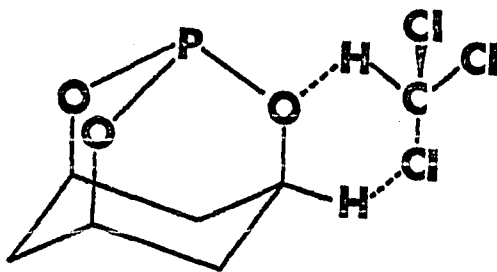
^aDimethyl sulfoxide.

^bProton peaks of solvent interfere.

do not hold for these systems, and that the chemical shifts of the methylene protons should be assigned by a comparison with similar molecules, thus placing H_{eq} downfield from H_{ax} . Supporting evidence for this assignment is the fine splitting observed in the upfield proton absorption of IV when the downfield proton is irradiated. This is attributed to a long range coupling of the axial proton with the phosphorus.

The P^{31} resonance spectrum of IV shows a quartet absorption at -137 p.p.m. downfield from 85% phosphoric acid in chloroform. The quartet arises from a coupling between the phosphorus nucleus and the three chemical equivalent methinyl protons in the cyclohexane moiety. The P^{31} resonance spectrum of the thiophosphate of IV shows an absorption at -64.0 p.p.m., and that of the phosphate an absorption at +10.4 p.p.m. This trend parallels that observed for $(C_2H_5O)_3P$, $(C_2H_5O)_3PS$, and $(C_2H_5O)_3PO$ (55).

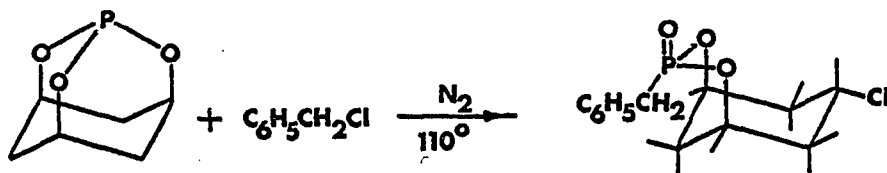
It was found that IV had an anomalously low dipole moment in chloroform (3.94 vs. 4.51 D. in dioxane). It is interesting that when $CDCl_3$ is the solvent used in the n.m.r. spectra of the compounds reported in Table 10, there is an anomalous deshielding for the majority of the protons. It is possible that these effects are due to hydrogen bonding between solvent molecules and the solute as depicted below. The net moment would thus be lowered by the opposite alignment of solute and solvent dipoles. That the chemical shift of the solute



protons occurs at lower fields compared to shifts observed in other solvents supports the postulate that hydrogen bonding with these compounds takes place in chloroform (52).

Michaelis-Arbuzov Reactions of IV

The Michaelis-Arbuzov rearrangement of trialkyl phosphites has been extensively studied by many workers (56-60). The first such rearrangement with the tricyclic phosphite IV was reported by Berlin, et al. (61). The reaction involved heating a mixture of IV and benzyl chloride at 110° under nitrogen, giving as the product the bicyclic phosphonate shown in the reaction below. The assigned equatorial



position of the Cl atom in the product was consistent with the infrared C-Cl stretching frequency ascribed to such a conformation as well as the substantial spin coupling of the axial proton to the axial protons observed on vicinal carbons as opposed to the small coupling generally associated with equatorial protons on vicinal carbons. From a knowledge of the overall dipole moment of the molecule and accepted bond moments, the dipole contribution of the chlorocyclohexane portion of the molecule was calculated. The dipole contribution of the phosphonate portion of the molecule was calculated and then positioned geometrically to add vectorially with the chlorocyclohexane contribution to give the total moment.

This same type of rearrangement occurs when IV reacts with benzyl p-toluenesulfonate via a sealed tube reaction, and when IV reacts with chlorotriphenylmethane in acetonitrile (62). The similarity in the n.m.r. spectra of these compounds and the analogous compound formed between IV and benzyl chloride (63) as well as the comparable steric requirements of these systems, is taken as supporting evidence for the conclusion that they have the same conformation. The proton n.m.r. spectra of these compounds along with the assignments of the absorptions are shown in Figure 10. That IV has indeed undergone a Michaelis-Arbuzov rearrangement in these reactions is further supported by the infrared spectra. A comparison with the benzyl chloride derivative shows no

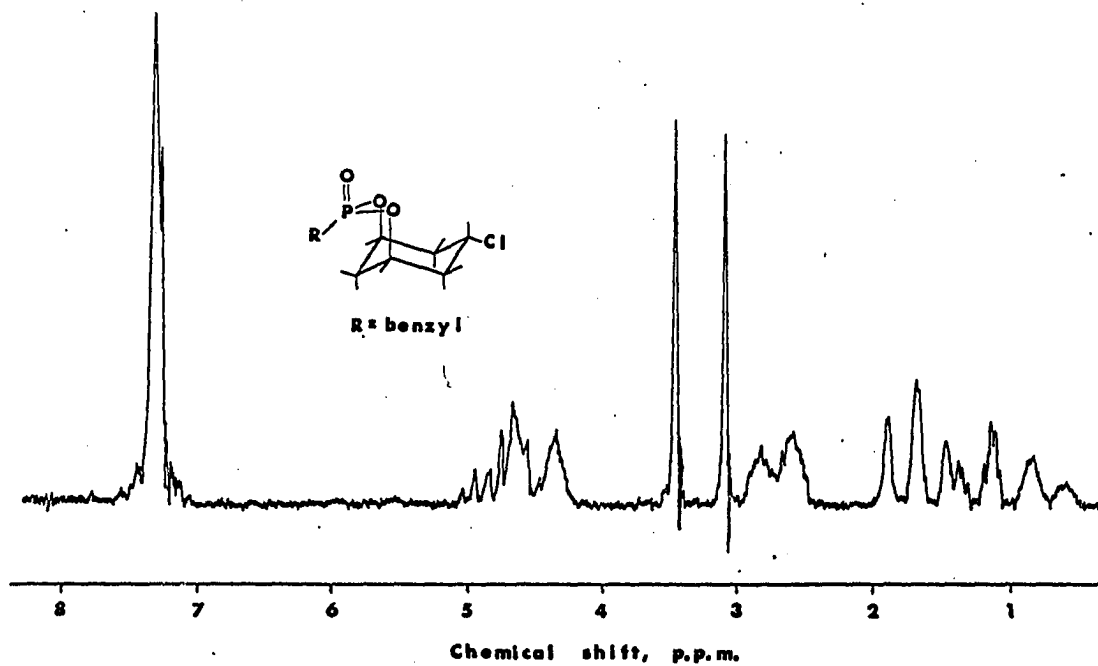
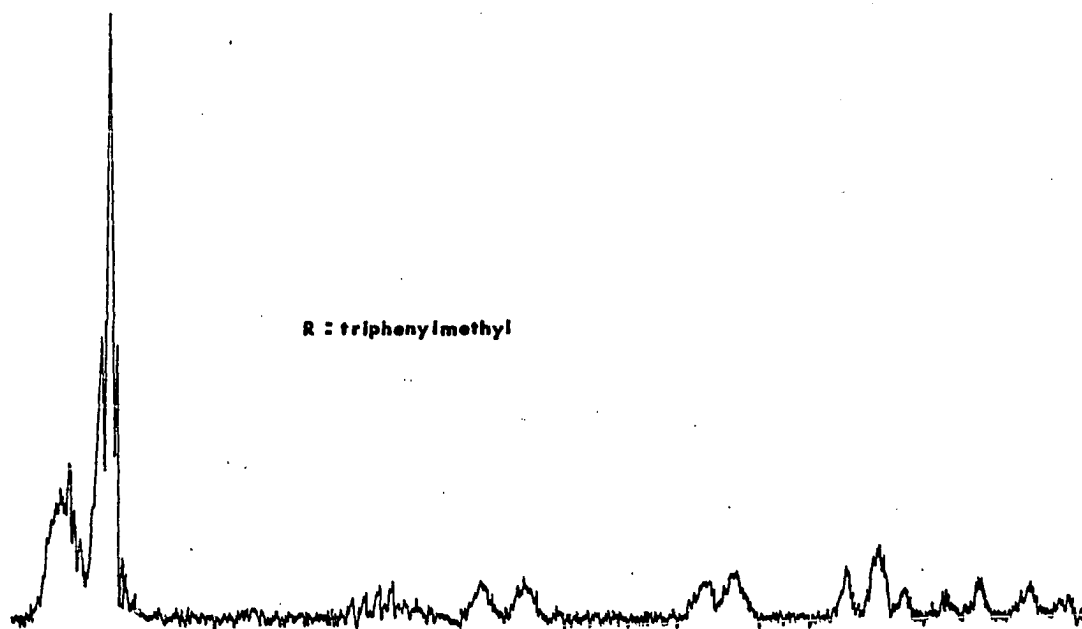
Figure 10. H^1 resonance spectra of Michaelis-Arbuzov products of IV in $CDCl_3$. All peaks downfield with respect to tetramethylsilane.

For R = benzyl the assignment is as follows: a singlet of five phenyl protons at -7.2 p.p.m.; a multiplet of one $ClCH$ proton at -5.0 p.p.m.; a doublet of two methinyl protons at -4.5 p.p.m.; a doublet of two methylene ($Ph-CH_2-$) protons at -3.2 p.p.m.; a doublet of two equatorial methylene protons at -2.8 p.p.m.; a triplet of two axial methylene protons at -1.8 p.p.m.; a doublet of one equatorial methinyl proton at -1.2 p.p.m.; and a doublet of one axial methinyl proton at -0.8 p.p.m.

For R = triphenylmethyl the assignment is as follows: a multiplet of fifteen phenyl protons at -7.9 p.p.m.; a multiplet of one $ClCH$ proton at -5.5 p.p.m.; a doublet of two methinyl protons at -4.5 p.p.m.; a doublet of two equatorial methylene protons at -3.1 p.p.m.; a triplet of two axial methylene protons at -2.0 p.p.m.; a doublet of one equatorial methinyl proton at -1.5 p.p.m.; and a doublet of one axial methinyl proton at -0.9 p.p.m. The peak at -7.6 p.p.m. is due to solvent impurity.

The assignment for R = benzyl was verified from a spectrum obtained at 100 Mc. (see reference 63).

66b



significant changes in the P=O (1260 cm.^{-1}) and P-O-C (1015 cm.^{-1}) frequencies. It is somewhat surprising that in spite of the low nucleophilic character and excellent ability to function as a leaving group, the p-toluenesulfonate anion attacks the cation formed from the benzyl carbonium ion and IV. These compounds possess no salt-like character as is confirmed by their negligible conductance values shown in methanol or acetonitrile solution (62).

It is interesting that when one drop of 70% perchloric acid is added to an acetone solution of an equimolar quantity of IV and H_2O , the cage phosphite ring system opens in such a manner that two isomers are formed. The proton n.m.r. spectra of the two isomers are shown in Figure 3. The P-H coupling constants for the two isomers, 730 and 781 c.p.s., are larger than any previously reported. These values are in contrast to $J_{\text{PH}} = 707 \text{ c.p.s.}$ reported for phosphorous acid (64).

The formation of two isomers is not expected in this reaction if a phosphonium salt intermediate is postulated as in the case of the Michaelis-Arbuzov rearrangement. The reason for postulating a phosphonium salt intermediate in the Michaelis-Arbuzov rearrangement can be seen in Figure 11 since the equatorial halide observed is predicted as a result of this mechanism. In addition, intermediate tetra-alkyl phosphonium halides have been isolated which supports the phosphonium mechanism (65).

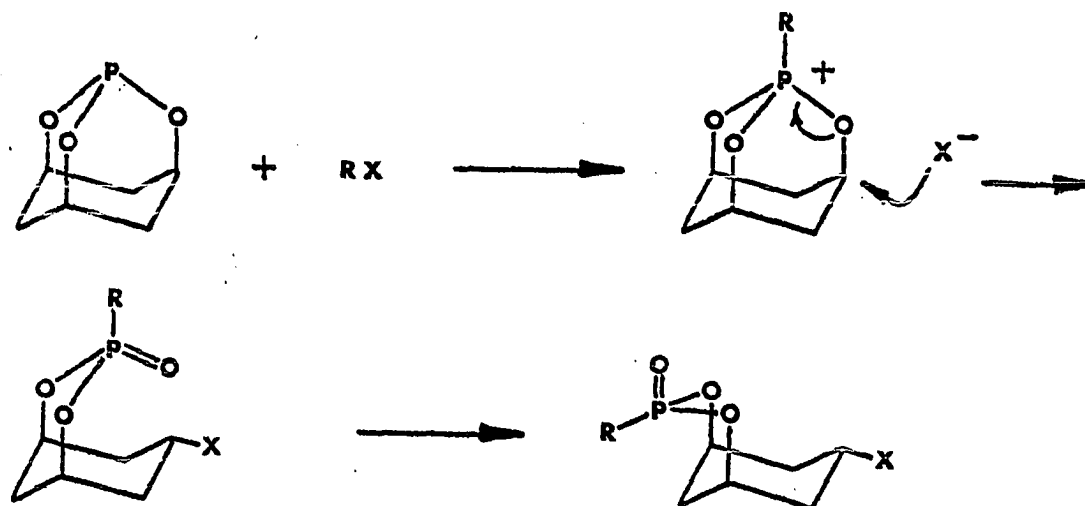


Figure 11. Proposed mechanism of the Michaelis-Arbuzov rearrangement of IV with alkyl halides

Two isomers could arise in the hydrolysis of IV from the two mechanisms postulated in Figure 12.

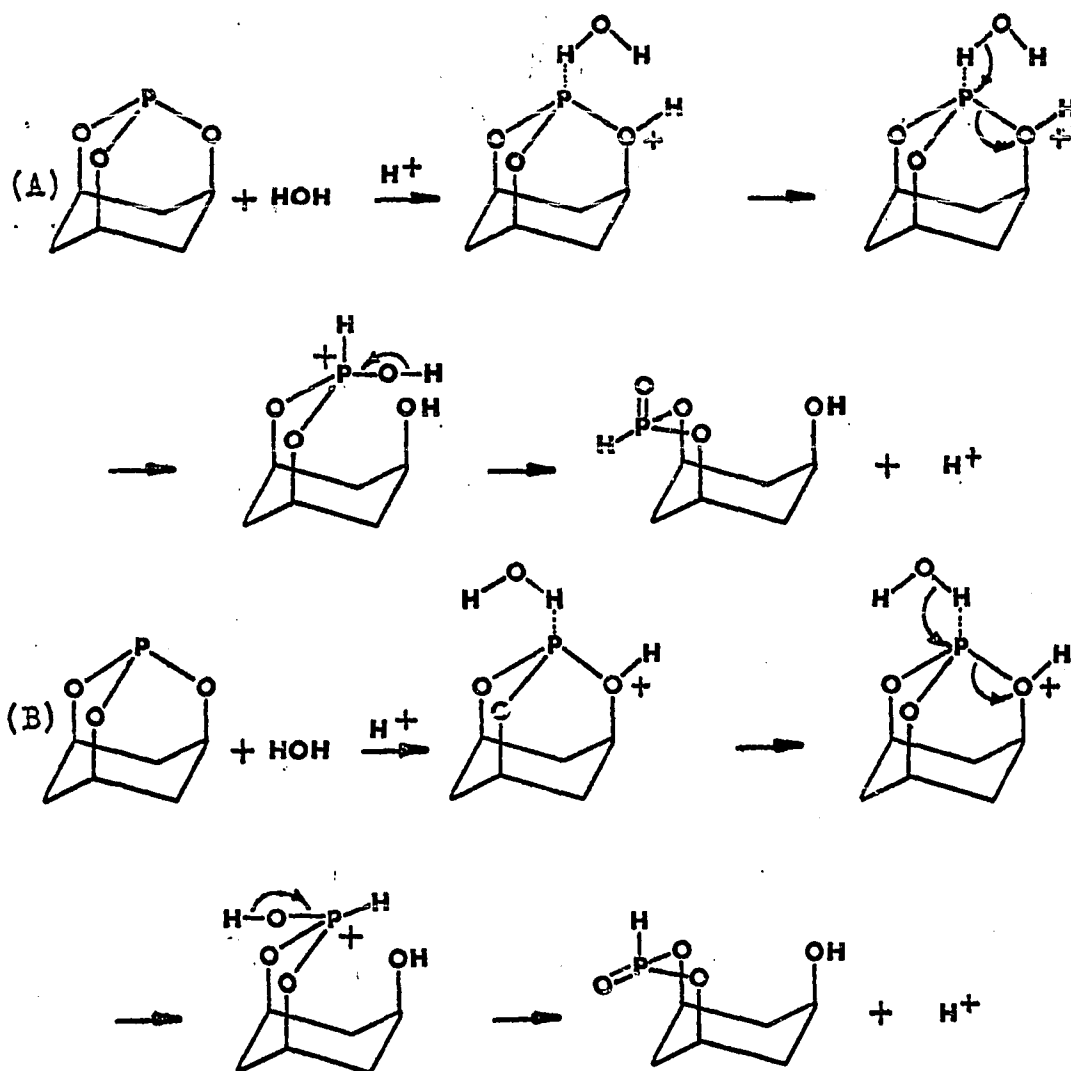
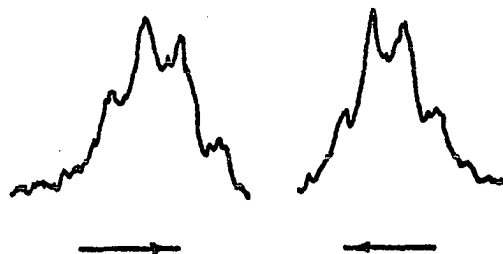


Figure 12. Proposed mechanism of hydrolysis of IV. Mechanism (A) gives rise to isomer A and mechanism (B) gives rise to isomer B

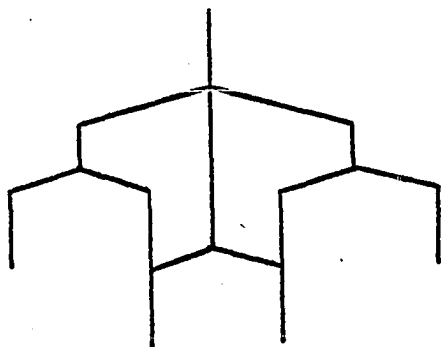
The n.m.r. spectra of the two isomers can be assigned to the two structures postulated in Figure 12. For isomer A the assignment is as follows: axial and equatorial protons at -1.98 and -2.46 p.p.m. (integration shows six such protons); proton on the alcoholic carbon at -4.32 p.p.m. (integration shows one proton); methinyl protons at -5.06 p.p.m. (integration shows two protons); the P-H proton at -7.20 p.p.m. (integration shows one proton); the alcoholic proton cannot be seen due to rapid exchange in D₂O. In dimethylsulfoxide the OH proton has been shown by deuteration experiments to absorb at the same field strength as one of the doublets due to the methinyl protons. As there are two different types of axial and equatorial protons in both structures, much fine structure in the n.m.r. spectra is observed.

The assignment of the n.m.r. spectrum of isomer B is the same as that for A with the only major difference being a more complicated splitting in the P-H hydrogen. When the proton absorption due to the P-H hydrogen is further resolved, each member of the doublet due to splitting by phosphorus becomes the 1:2:2:1 quartet shown in Figure 13. This could arise from additional coupling of the P-H proton with the two methinyl protons to give a triplet and a further coupling with the axial proton directly beneath the P-H proton to give a doublet of triplets. Such a coupling can give rise to overlap of the two triplets to give the necessary 1:3:3:1 quartet. The P-H

bond is postulated to be colinear with the axial C-H for such long-range coupling to take place. Examples of long-range coupling wherein colinearity of C-H links is an important factor in the magnitude of proton-proton coupling is discussed elsewhere (54,66,67).



The expanded P-H proton spectrum observed by sweeping the magnetic field in both directions through the absorption



The uncoupled P-H proton

A 1:2:1 triplet arising from coupling with the two methinyl protons

A 1:3:3:1 quartet arising from further coupling with the colinear axial methylene proton

Figure 13. H' resonance spectrum of P-H in isomer B

If the proton on the alcoholic carbon were in an axial position, a splitting on the order of 5 to 8 c.p.s. would be expected due to coupling with the two methylene axial protons (53,63). As this is not observed the OH group is tentatively assigned to the axial position.

It is interesting that the divalent zinc and cadmium ions form four coordinate complexes with IVH_2O thus completing their inner coordination sphere, but the complexes of the divalent manganese and iron ions contain only five molecules

of IVH_2O , the sixth coordination site being occupied by a molecule of H_2O . This may be due to an inability to pack six molecules of IVH_2O around a metal ion because of their bulk. The formulations postulated for these complexes is supported by elemental analyses. The infrared spectra of these complexes reveal that only one isomer (isomer A) is coordinated to a metal ion.

It is assumed that coordination is through the phosphoryl oxygen, although the $\text{P}=\text{O}$ stretch in the infrared is not affected to a great extent. Assuming some pi-bond character in the $\text{P}-\text{O}$ bond, Cotton, et al. (68), have postulated three effects of complex formation on the $\text{P}-\text{O}$ bond order. (1) If the oxygen atom forms a sigma-bond with the metal atom there will be an enhancement of the $\text{P}-\text{O}$ sigma-bond. This would result in an increase in the $\text{P}-\text{O}$ stretching frequency. (2) This same effect will cause a decrease in the p-pi d-pi back bonding from the oxygen atom to the phosphorus atom, thus lowering the $\text{P}-\text{O}$ stretching frequency. (3) If the transition metal ions under consideration have low-energy filled d-orbitals, an electronic repulsion may result in which the p-pi electrons of the oxygen atom are forced toward the empty d-pi orbitals of the phosphorus atom. The result would be an increase in the $\text{P}-\text{O}$ stretching frequency.

The second effect was postulated by Cotton (68) to be predominant in $\text{R}_3\text{P}=\text{O}$ complexes. It is conceivable that in the

transition metal complexes of IVH₂O (isomer A), the other two oxygen atoms adjacent to phosphorus have an overriding effect because of their high electronegativity. If this is the case, it may be rationalized that upon coordination, the three effects postulated by Cotton might be of the same magnitude and small, thus resulting in very little or no shift of the P-O stretching frequency in the infrared spectra of the complexes of IVH₂O.

Phosphonium Salts of IV

Although the reactions of trialkyl phosphites with a carbonium ion and a nucleophilic anion involve the Arbuzov reaction, similar reactions with nonnucleophilic anions have been limited to the salts formed from the reaction of trialkyl phosphites and $[(\text{CH}_3\text{CH}_2)_3\text{O}]\text{BF}_4$ or $[(\text{C}_6\text{H}_5)_3\text{C}]\text{BF}_4$ (69,70). That the cage remains intact upon the reaction of IV with carbonium perchlorates and tetrafluoroborates is verified by comparing infrared and n.m.r. spectra of these compounds with the more complicated spectra of products obtained from the Michaelis-Arbuzov reactions of IV. The conductivity data in Table 7 support the salt-like nature of the phosphonium compounds. These compounds are in general stable to heat and moist air and can be prepared in relatively high yields, which is in marked contrast to the instability, low yields, and lower melting points of the previously reported analogous salts of open-chain phosphites. Although the rigid and

symmetrical cations contribute to the high lattice energies associated with compounds of polycyclic phosphites (26), the increased stabilization of the cation in solution can only be attributed to a stronger P-O bond. Apart from changes in hybridization around the phosphorus atom which are undoubtedly minimal upon quaternization of IV, the main contribution to the increased stability stems from the reduced steric hindrance to coordination of a triphenylmethyl or ethyl carbonium ion as well as to the greater polarity of the phosphite moiety (37).

From Table 11 it can be seen that there is a variation of the value of J_{POCH} with the chemical shifts of the protons on C_β in IV and its derivatives, in striking contrast to a similar series of compounds of trimethyl and triethyl phosphite. It is also significant that a plot of these parameters for protons on C_β and C_γ (axial) in IV and its derivatives is reasonably linear as shown in Figure 14. Whereas the phosphorus-acceptor bond in all of the compounds can be considered to be purely sigma in character, it is tentatively concluded that the rise in J_{POCH} stems from an increase in s character of the three P-O bonds as the phosphorus-acceptor bond increases in p character. This rise in s character of the P-O bond is attributable to the increasing electronegativity of the acceptor groups wherein a lone pair of electrons <

$\text{B}(\text{CH}_3)_3 < \text{BH}_3 < \text{CH}_3\text{CH}_2 < (\text{C}_6\text{H}_5)_3\text{C}$. The increase in the

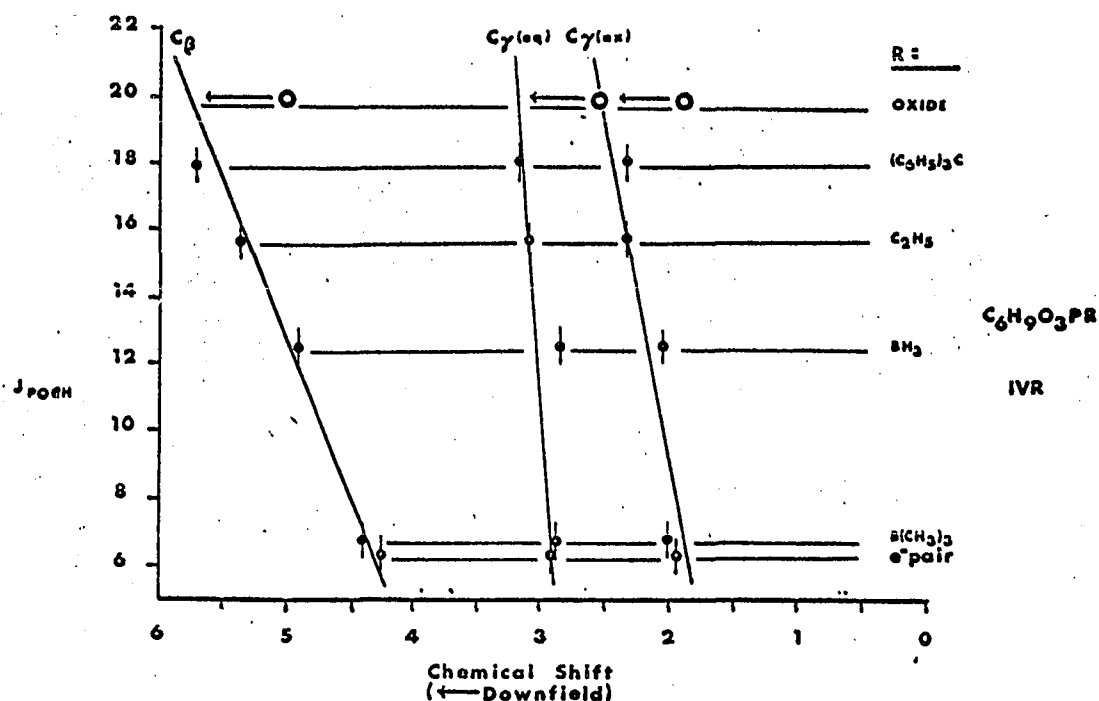


Figure 14. Spin coupling (c.p.s.) of P to H on C_β and C_γ carbons (J_{PCH}) vs. chemical shift (p.p.m. with respect to tetramethylsilane) of protons in IV ($C_6H_9O_3P$) and its $B(CH_3)_3$, BH_3 , C_2H_5 , $(C_6H_5)_3C$, and oxide derivatives

electronegativity of these acceptor groups is compatible with the observed downfield trend of the C_β and C_γ (axial) protons for this series of derivatives since an increasingly positive charge accumulates on the phosphite moiety.

Table 11. Phosphite derivative proton chemical shifts (p.p.m. vs. $\text{Si}(\text{CH}_3)_4$)^a

Compound	C_β	C_γ ^b	C_γ	J_{POCH} c.p.s.
$(\text{CH}_3\text{O})_3\text{P}$	3.69			11.35
$(\text{CH}_3\text{O})_3\text{PB}(\text{CH}_3)_3$	3.69			9.60
$(\text{CH}_3\text{O})_3\text{PBH}_3$	3.70			11.00
$[(\text{CH}_3\text{O})_3\text{PC}(\text{C}_6\text{H}_5)_3]\text{BF}_4$	3.90			10.85
$(\text{CH}_3\text{O})_3\text{P}=\text{O}$	3.46			10.65
$(\text{CH}_3\text{CH}_2\text{O})_3\text{P}$	3.82	1.20		7.50
$[(\text{CH}_3\text{CH}_2\text{O})_3\text{PCH}_2\text{CH}_3]\text{BF}_4$	4.50	1.42		7.45
$[(\text{CH}_3\text{CH}_2\text{O})_3\text{PC}(\text{C}_6\text{H}_5)_3]\text{BF}_4$	4.33	1.20		6.70
$(\text{CH}_3\text{CH}_2\text{O})_3\text{P}=\text{O}$	4.05	0.99		6.84
$\text{C}_6\text{H}_9\text{O}_3\text{P IV}$	4.24	2.90	1.93	6.3
$\text{C}_6\text{H}_9\text{O}_3\text{PB}(\text{CH}_3)_3$	4.38	2.87	1.98	6.7
$\text{C}_6\text{H}_9\text{O}_3\text{PBH}_3$	4.88	2.85	2.05	12.5
$[\text{C}_6\text{H}_9\text{O}_3\text{PCH}_2\text{CH}_3]\text{BF}_4$	5.37	3.08	2.33	15.7
$[\text{C}_6\text{H}_9\text{O}_3\text{PC}(\text{C}_6\text{H}_5)_3]\text{BF}_4$ (or ClO_4^-)	5.45	3.18	2.34	18.0
$\text{C}_6\text{H}_9\text{O}_3\text{P}=\text{O}$	5.00	2.56	1.90	20.0

^aGreek subscripts refer to the position of the proton-bearing carbon atom with respect to phosphorus.

^bWhere two values are reported, the higher refers to the equatorial and the lower to the axial hydrogen.

The interpretation presented for the results depicted in Figure 14 has been employed by Kaesz, et al. (71), to explain trends in a number of trialkyl phosphine derivatives. However, no linear correlations of phosphorus-proton coupling constants with the proton chemical shifts in the trialkylphosphines are apparent. It is evident that the structural rigidity of IV and its derivatives precludes any significant conformational changes upon coordination of the phosphite which may be of importance in open-chain phosphines.

Compounds of IV in which the phosphorus atom can pi-bond to the acceptor group consistently fall to the right of the lines in Figure 14 when similarly plotted. The phosphate derivative is shown for comparison since an unusually large amount of pi-bonding is postulated to occur in this compound (72).

No distinct downfield trends are noted in Table 11 for the protons in trimethyl and triethyl phosphite derivatives with increasing electronegativity of the sigma-bonding acceptor group. The anomalous constancy of J_{POCH} in these respective derivatives cannot be interpreted by the simple arguments presented for the derivatives of IV. It is possible that any change in coupling constant brought about by varying the acceptor group is compensated by a structural change due to the greater flexibility of the open-chain phosphite systems.

Transition Metal Complexes of IV

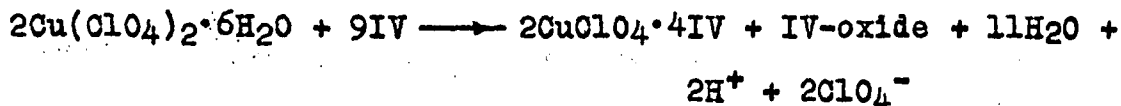
The coordination compounds of IV are listed in Table 12, and will be discussed in the order indicated. The formulations postulated are supported by elemental analyses and molar conductivities. It is interesting to note that in almost all cases, maximum coordination is achieved with only IV in the coordination sphere. This would tend to bear out one of the premises that constraint of the alkoxy moiety in trialkyl phosphites renders possible maximum coordination of a metal ion due to the reduction of ligand-ligand steric repulsions.

Table 12. Transition metal complexes of IV

CuClO ₄ ·4IV, CuNO ₃ ·4IV, AgClO ₄ ·4IV, AgNO ₃ ·4IV, AuCl·IV
Ni(ClO ₄) ₂ ·6IV, Ni(ClO ₄) ₂ ·5IV·H ₂ O, Ni(NO ₃) ₂ ·5IV·H ₂ O, Ni·4IV
PtCl ₂ ·2IV, PdCl ₂ ·2IV·2IVH ₂ O
CoClO ₄ ·5IV, Co(ClO ₄) ₃ ·6IV, (Co·5IV) ₂ (Co·4NO ₃), Co(NO ₃) ₃ ·6IV

Copper, silver and gold complexes of IV

When a solution of a copper(II) salt is reacted with IV, an oxidation-reduction takes place wherein a copper(I) complex and the oxide of IV is formed.

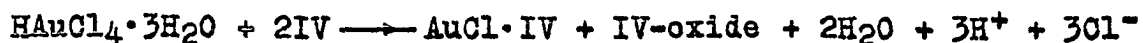


The impetus for this reaction is probably the formation of a more stable copper(I) cation by IV than the possible

complexation of a copper(II) cation by IV. The colorless complexes are probably tetrahedral complexes and in the valence bond picture would utilize sp^3 hybrid orbitals of the metal. There might also be appreciable stabilization due to $d-pi$ $d-pi$ bonding. It is noteworthy that in the copper nitrate complex four molecules of IV are found in the coordination sphere, whereas with triphenylphosphine only two molecules enter the coordination sphere (73).

The colorless silver complexes are formed in 100% yield and are quite stable to visible light. The geometry of these four-coordinate complexes is probably also tetrahedral.

The gold complex of IV is quite similar to other complexes of gold with phosphorus-containing ligands (1,18). The reaction involves the reduction of the Au(III) ion in $HAuCl_4 \cdot 3H_2O$ to the Au(I) ion, the oxidation product being the oxide of IV.



If a noncoordinating anion were used in place of chloride, maximum coordination would probably be achieved with only IV in the coordination sphere. The colorless complex is probably linear utilizing sp or dp hybrid orbitals.

Nickel complexes of IV

The ease with which a maximum coordination number of six is attained in the formation of the $(Ni \cdot 6IV)^{+2}$ ion is striking as well as its diamagnetism. Although the structure determin-

ation by means of X-ray crystallography has not been completed at this time, it is of interest to speculate briefly on the configuration of this ion. Undistorted octahedral symmetry would require promotion of the electrons in the upper doublet of the 3d metal orbitals to the 4s level with consequent pairing in view of the diamagnetism. Tetragonal distortion would result in splitting the e_g metal doublet; however the energy must be large enough to pair the electrons in the d_{z^2} orbital. In a trigonal distortion of the octahedron, a set of molecular orbitals having the relative energies shown in Figure 15 can be obtained from the resultant D_{3d} trigonal antiprism. Such a scheme can indeed account for the diamagnetism of the compound. Schaffer and Jorgensen have recently shown that for such an orbital scheme, the distance from the nickel atom to each triangular array of ligand atoms in the elongated trigonal antiprism shown in Figure 16 must be 1.5 or more times as great as it is in a pure octahedron. If such a large distortion indeed occurs, the band at $365\text{ m}\mu$ could be the result of a transition from a sigma ligand orbital to the empty antibonding sigma metal orbital. Although this postulate is attractive, it leaves unexplained any reason for the distortion.

The two yellow nickel complexes prepared from the hydrated salts are still somewhat controversial. The elemental analyses, molar conductivities, and yields indicate five molecules of IV, and the infrared spectra reveals a band in

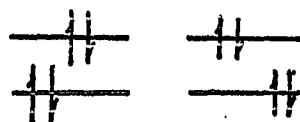


Figure 15. Molecular orbital energy levels derived for a trigonal distortion of $(\text{Ni} \cdot 6\text{IV})^{++}$. (C. Schaffer, University of Copenhagen, and Chr. K. Jorgensen, Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Private communication. 1965)

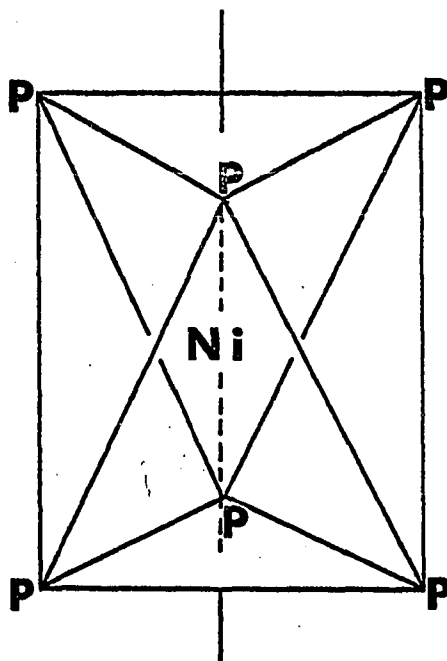
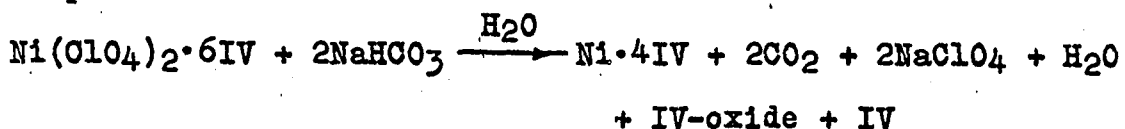


Figure 16. Elongated trigonal antiprism resulting from the trigonal distortion of $(\text{Ni} \cdot 6\text{IV})^{++}$

the OH region (3500 and 1625 cm^{-1}) even after drying under vacuum at 110° for 24 hours. It is still undetermined whether this water molecule is coordinated to the nickel or is a water of crystallization. It is remarkable that the $(\text{Ni} \cdot 5\text{IV} \cdot \text{H}_2\text{O})^{++}$ and $(\text{Ni} \cdot 6\text{IV})^{++}$ cations have similar solubility properties, identical n.m.r. spectra, and similar visible and infrared spectra with the exception of the OH absorptions.

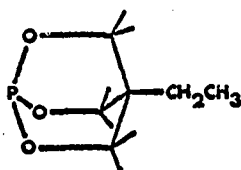
The ease with which the $(\text{Ni} \cdot 6\text{IV})^{++}$ species is reduced is undoubtedly coupled with the fact that the intense band in the $365 \text{ m}\mu$ region represents facile promotion of electrons from sigma phosphorus orbitals to empty metal orbitals. That the zero-valent nickel complex is indeed stable is reflected in its high yield and the relatively mild conditions under which it is formed. In contrast to $\text{Ni} \cdot 4\text{P}(\text{OMe})_3$ and $\text{Ni} \cdot 4\text{P}(\text{OEt})_3$ (74), the analogous complex with IV is stable in air and moisture. The reaction shown below differs from that reported by Vinal and Reynolds (8) in that the reduction is carried out on an isolated hexacoordinate nickel(II) complex.



Platinum and palladium complexes of IV

The only isolated platinum complex that could be characterized was trans- $\text{PtCl}_2 \cdot 2\text{IV}$. The stoichiometry was determined by elemental analyses and the geometry was determined

indirectly by an n.m.r. technique. The insolubility of the complex in most common solvents, which might in itself be an indication of a trans-configuration, necessitated the use of another caged phosphite ligand, VI, that would conceivably react in a similar manner as IV with platinum(II) and give complexes which are much more soluble than those of IV, thus allowing the requisite concentration for the n.m.r. study. It has been reported by Jenkins and Shaw (75) that phosphorus-phosphorus coupling in a platinum complex containing phosphine ligands is different depending on whether the complex is in



VI

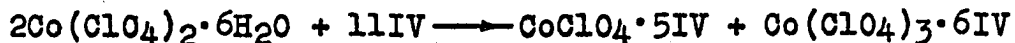
the cis- or trans-configuration. For example, the H^1 resonance of the methyl protons in free dimethylphenylphosphine is a symmetrical doublet due to spin-spin interaction with the phosphorus nucleus, but when two molecules of this phosphine are present in a complex in trans position to one another, then this resonance is not a doublet but is usually a very well defined and narrow 1:2:1 triplet arising from phosphorus-phosphorus coupling. The methylene protons in free VI absorb as a doublet in the H^1 n.m.r. spectrum due to coupling with

the phosphorus nucleus and as a well defined triplet in the platinum complex. This would indicate $\text{PtCl}_2 \cdot 2\text{VI}$ to be in a trans-configuration and would therefore support the trans-configuration postulated for $\text{PtCl}_2 \cdot 2\text{IV}$. Maximum coordination with only IV in the coordination sphere is not achieved probably because of the good coordinating properties of the chloride ion.

The palladium complex is still somewhat controversial. The elemental analyses and infrared spectra indicate two molecules of IV and two molecules of IVH_2O to be present. The compound is extremely insoluble in most common solvents and decomposes in water. If the complex is extracted with methanol over a period of 24 hours, the molecules of IVH_2O are removed. However, the remaining complex containing only IV ligands has not been successfully characterized as yet.

Cobalt complexes of IV

It is remarkable that the reaction of IV with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ seems to involve a quantitative disproportionation to a pentacoordinate cobalt(I) and a hexacoordinate cobalt(III) complex.



The cobalt(III) complex is expected to be diamagnetic on the basis of its d^6 electronic configuration since in a strong octahedral field the six electrons will be paired in the t_{2g} level. The complex is one of the first known cases of a

colorless cobalt(III) complex along with the analogous complex of III (22). If it can be assumed from the energy level diagram shown in Figure 17 (76) that the bands at 320 and 298 $m\mu$ are the spin-allowed ${}^1A_{1g}(t_{2g})^6 \longrightarrow {}^1T_{1g}(t_{2g})^5(e_g)$ and ${}^1A_{1g}(t_{2g})^6 \longrightarrow {}^1T_{2g}(t_{2g})^5(e_g)$ transitions, respectively, then the following calculation yields a value for Dq . Assuming that the ratio of the parameters $F_2/F_4 = 9.3$ for the $Co(en)_3^{+3}$ ion (77) is also valid for the $(Co \cdot 6IV)^{+3}$ ion, a value of 33.3 $cm.^{-1}$ for F_4 is obtained by solving simultaneously the equations for the strong-field approximation (77)

$$E({}^1T_{1g}) = -35F_4 + 10Dq$$

and

$$E({}^1T_{2g} - {}^1A_{1g}) = 16F_2 - 115F_4 + 10Dq.$$

The Dq value arrived at in this manner, 3246 $cm.^{-1}$, is very close to that of the $Co(CN)_6^{-3}$ ion which is 3350 $cm.^{-1}$ (78). The fact that IV produces as large a crystal field as the cyanide ion in the Co^{+3} ion supports the postulate that some type of multiple bonding is involved in the complexation of IV to some transition metal ions.

The possibility of trigonal bipyramidal symmetry for the $(CoIV_5)^+$ cation is supported by the spectral data shown in Table 6. The strong band at 342 $m\mu$ may well represent the $(e'')^4(e')^4(a_1')^0 \longrightarrow (e'')^4(e')^3(a_1')^1$ transition in the molecular orbitals of the partly filled shell in an MX_5 chromophore (79). Confirmation of the trigonal bipyramidal configuration

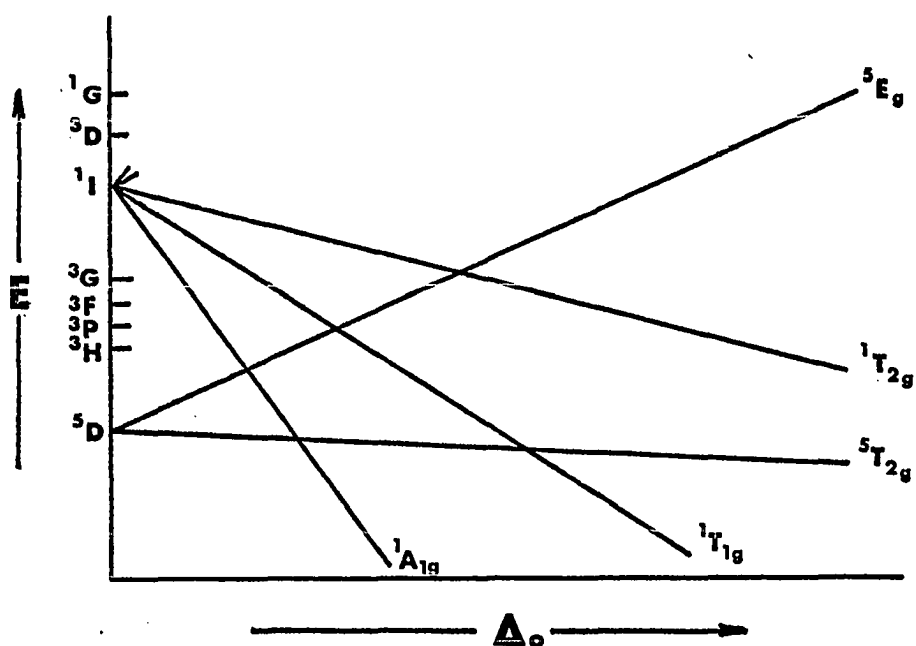
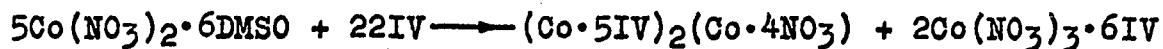


Figure 17. Energy level diagram for Co^{+3}

awaits X-ray diffraction studies.

When an identical reaction was carried out between IV and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a mixture of purple and white crystals resulted which were extremely hygroscopic and resisted separation and purification. In order to see if the nitrate complexes could be made, an ion exchange experiment was carried out in which both modifications of the cobalt perchlorate complexes of IV were passed through an Amberlite 401 chloride ion exchange resin. The resulting solutions were then titrated potentiometrically with standard silver nitrate solution. The results indicated within 1% error that both of the nitrates could be synthesized.

In order to carry out the reaction under completely anhydrous conditions, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{DMSO}$ was used as the starting material. When IV was reacted with this cobalt complex, a white solid contaminated with a small amount of purple solid formed. The colorless modification is $\text{Co}(\text{ClO}_4)_3 \cdot 6\text{IV}$ and the purple modification was shown by the visible spectrum to contain the $(\text{Co} \cdot 5\text{IV})^+$ cation and the $(\text{Co} \cdot 4\text{NO}_3)^{-2}$ anion (80). The purple complex is quite hygroscopic and decomposes rapidly in air. The following reaction is proposed.



Transition Metal Complexes of Open-Chain Trialkyl Phosphites

The unusually great coordinating powers of III and IV were initially rationalized on the basis of significantly reduced steric hindrance to coordination and consequent low ligand-ligand repulsion of III and IV compared to trialkyl phosphites as revealed by scale models. In order to determine the relative importance of these steric considerations, it became of interest to attempt to prepare complexes of open-chain trialkyl phosphites. To reduce complications due to anion coordination, metal perchlorates were employed.

It is interesting that three solid complexes could be isolated and characterized, and that the isolation of other solid complexes of trialkyl phosphites will undoubtedly come about using different preparative techniques. All of the compounds appear to be reasonably stable in air although the odor of trimethyl phosphite could be detected over the yellow-orange nickel compound. That the two nickel complexes have different stoichiometries ($\text{Ni}(\text{ClO}_4)_2 \cdot 5\text{P}(\text{OMe})_3$ and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{P}(\text{OEt})_3$) might be due to a loss of trimethyl phosphite by that complex. It appears that previous attempts to isolate metal ion complexes of open-chain phosphites have been hindered by the presence of the coordinating halide ion.

Although scale models of the reported complexes reveal a high degree of ligand-ligand repulsion, some degree of configurational stability can be attained by orienting the

alkoxy groups on the phosphorus atom such that the R group is as far as possible from the metal atom. It is possible that free rotation of the alkoxy groups is thus restrained upon coordination of the phosphorus atom in order to minimize ligand-ligand repulsion and allow the closest approach of the phosphorus to the metal atom.

AREAS FOR FURTHER INVESTIGATION

Ligand IV and Derivatives

The overall yield, about 18%, in the preparation of IV is not very satisfying. The use of different stereospecific catalysts, such as rhodium, may give a much higher yield of cis-1,3,5-cyclohexanetriol in the hydrogenation of phloroglucinol dihydrate.

There is still much to be done with the hydrolysis product of IV (IVH_2O) aside from the structure determination by X-ray crystallography. The effect of acidity on the formation of IVH_2O from IV should be investigated as this may give some insight into the mechanism of the reaction. The physical and chemical properties of the coordination compounds of IVH_2O are still to be determined. The P^{31} n.m.r. spectra may distinguish which atom in the molecule is bonding to the metal ion. As all of the coordination compounds of IVH_2O are obtained by a direct reaction of IV with the hydrated metal perchlorate, an investigation should be carried out using isomer A and isomer B as ligands. This would probably necessitate the use of anhydrous metal complexes, such as the dimethylsulfoxide or pyridine complexes.

Transition Metal Complexes of IV

The structures and stoichiometries of the coordination compounds of IV with the transition metal halides CoCl_2 ,

NiCl_2 , and CuCl_2 , are still to be determined along with any other transition metal halide complexes of IV that might be prepared. It is significant that solid compounds are obtained in view of the intractable oils for the reactions between cobalt and nickel halides with various $(\text{RO})_3\text{P}$ ligands previously reported (1).

Further attempts should also be made to prepare complexes of IV with chromium(III), manganese(II), iron(II) and iron(III). This would probably involve using anhydrous conditions and more vigorous reaction conditions than those employed in this work. Such a series of transition metal complexes along with those already synthesized might furnish information concerning the electronic environment required about a metal ion for a good coordination of phosphorus-containing ligands. A correlation such as this would yield qualitative insight into the role of multiple bonding in phosphorus-metal bonds.

The most direct method of determining the type of bonding that takes place in the complexes of IV would be a measure of phosphorus-metal stretching frequencies. With the far infrared equipment now available, such measurements are possible and should be carried out on the coordination compounds of IV.

Transition Metal Complexes of Open-Chain Trialkyl Phosphites

This field of research is completely open to investigation except for the initial research done in this work. As

it has been previously reported, trialkyl phosphites are quite susceptible to hydrolysis especially in the presence of acid (81). The author suggests that completely anhydrous conditions be employed in the future. This might require more vigorous reaction conditions than those employed in this work. It is also possible to carry these reactions out neat, thus eliminating the possibility of solvent interaction.

By preparing complexes of the same transition metal ion with different trialkyl phosphites, the importance of steric interactions in these systems upon coordination to a metal ion should be revealed. For example, it might be shown that upon coordination to a metal ion the alkoxy groups can orient themselves in such a manner that the phosphite ligands do not sterically interact and give rise to ligand-ligand repulsion.

The high solubility in organic solvents of the complexes thus far prepared, gives rise to the interesting possibility of investigating the nature of the electronic environment about the phosphorus nucleus upon coordination to a metal ion by means of P^{31} n.m.r. spectroscopy. Such a study was prevented in the case of complexes of IV due to their low solubility.

The Arsenic Analog of IV

As the literature is completely void of information concerning the isolation of transition metal complexes of trialkyl arsenites, the same type of investigation should be

carried out on the arsenic analog of IV as was carried out on IV. The main problem here will be to carry out investigations under completely anhydrous conditions since the compound is quite susceptible to hydrolysis.

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